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CONDUCTANCES, DENSITIES, AND FLUIDITIES OF SOLUTIONS OF SILVER NITRATE AND OF AMMONIUM NITRATE AT 35°[1]

BY A. N. CAMPBELL, A. P. GRAY[2], AND E. M. KARTZMARK

ABSTRACT

The equivalent conductances of concentrated solutions of ammonium and silver nitrates have been determined up to saturation at 35.00°C. with a probable error of 0.1%. The equivalent conductances behave in a normal manner for strong electrolytes in aqueous solution, being approximately linear with the first power of the concentration, though slightly convex to the concentration axis. The viscosities and fluidities of these same solutions have been determined both at 25.00°C. and 35.00°C. with a probable error of 0.2%. Ammonium nitrate solutions exhibit the phenomenon of "negative viscosity" which tends to disappear at higher temperatures, the viscosity minimum or fluidity maximum shifting towards higher dilution. The silver nitrate fluidities decrease continuously with concentration, the curve showing less tendency to linearity at high concentrations than that for ammonium nitrate. The densities of the solutions at both temperatures have been determined with an apparent error of 0.02%. Apparent molal volumes have been calculated from these figures at 35.00 C. The concentrations of the saturated solutions of both salts at 25.00 C. and 35.00°C. have been determined by the conductance method and are in good agreement with the published data. The average temperature coefficients of fluidity and conductance for both salts have been evaluated between 25.00°C. and 35.00 C. and an approximate constancy of the ratio of fluidity coefficient to conductance coefficient has been observed beyond 2 molar. The ratios appear to have the mean value of 1.12 for both salts in spite of a considerable difference in the individual coefficients.

THEORETICAL

This paper is a record of experimental work on the conductance, density, and viscosity of solutions of ammonium nitrate and of silver nitrate at 25° and 35°C. It is part of a general campaign of work on the conductance of strong solutions of salts (3).

Previous Work on the Present Problem

Ammonium Nitrate

Although an enormous amount of conductance work of extremely high accuracy has been reported in the literature since 1930, it appears that ammonium nitrate has been largely neglected. No data could be found in the literature for ammonium nitrate conductance except those quoted in the International Critical Tables for 18.00°C. (8) and that of Scatchard and Prentiss for 10.0°C. (14). The conductance of this salt therefore is not known in dilute solution either at 25.00°C. or 35.00°C., although the limiting conductances may be obtained from the limiting ionic conductances and their temperature coefficients at infinite dilution.

The only data to be found in the literature for the viscosity of ammonium nitrate solutions are those obtained by Getman in 1908 (5).

[1] *Manuscript received January 8, 1953.*
Contribution from the Chemistry Department of the University of Manitoba, Winnipeg, Manitoba.

[2] *Holder of Cominco Research Fellowship, 1951-1952.*

Silver Nitrate

The conductance of this salt has been very accurately determined by Shedlovsky in the region up to 0.1 *N* (15), at 25.00°C. It has been pointed out by MacInnes, Shedlovsky, and Longsworth (12) that silver nitrate is somewhat "abnormal" in that it shows no deviation from the Onsager straight line slope up to a concentration of 0.002 *N*, whereas for the alkali halides agreement to 0.001 *N* is exceptional. They also point out that the observed limiting slope of the transference number of silver nitrate is of opposite sign to that predicted on the basis of the theory. A complete investigation over the range of concentrated solutions at 25° and 95°C. has been made by us (3).

Some very accurate data for the viscosity of silver nitrate solutions at 25.00°C. and 0.00°C. have been obtained by Jones and Colvin (10) up to a concentration of 5 molar.

EXPERIMENTAL

Purification of Materials

Conductance measurements in the dilute region are very greatly influenced by the presence of even minute amounts of impurities in the salts. In this work, however, the specific conductances are so high that the solvent correction is completely negligible. Further, since the over-all accuracy expected is no better than 0.1%, the purity of the salts is not nearly as critical in these concentrated solutions. Nevertheless, the best materials available were purified and dried according to the following methods:

(i) *Ammonium Nitrate*

This was part of a bulk lot obtained from the Consolidated Mining and Smelting Company during the last war. The salt was cycled through at least three crystallizations from water followed by a final recrystallization from water and ethanol. It was then placed in an oven at 80°C. for 24 hr., removed, finely ground in an agate mortar, and replaced in the oven for an additional 24 hr. The grinding was repeated several times to ensure the absence of any occluded mother liquor and the salt was finally stored over sulphuric acid until required.

(ii) *Silver Nitrate*

The silver nitrate was that supplied by the Johnson, Matthey and Mallory Company, and was adequately pure but for the presence of some water. It was felt that nothing would be gained by recrystallization and the salt was carefully fused in a platinum dish, ground in an agate mortar to a fine powder, and stored over sulphuric acid in a darkened space. The resulting salt was pure white in appearance, and showed no visible evidence of decomposition.

(iii) *Potassium Chloride*

A good reagent grade potassium chloride was recrystallized twice from water and fused in a platinum dish. The salt was then ground very finely and kept over sulphuric acid.

(iv) *Conductance Water*

The specific conductivity of this water was of the order of 1.5×10^{-6} mhos

which indicated a purity entirely adequate for the concentrated solutions and for the calibration of the viscometers.

Preparation of the Solutions

With the exception of the four saturated solutions, all were made up by weight. The weights were calibrated. The density of the air was calculated from a knowledge of the temperature, humidity, and atmospheric pressure, and corrections to vacuum were made in every case.

The concentrations of the saturated solutions were determined by dilution of a weighed amount of the solution to a convenient lower concentration by weight. The specific conductance of the dilute solution was then determined and from a graph of specific conductance versus weight per cent, at 25°C. the weight per cent of the diluted solution was found.

Temperature Control

All thermometers were calibrated against a platinum resistance standard. The 25°C. thermostat showed no variance in temperature detectable on a

TABLE I

DENSITIES AND SPECIFIC AND EQUIVALENT CONDUCTANCES OF AQUEOUS AMMONIUM NITRATE SOLUTIONS AT 35.00°C.

Concentration		d_4^{35},	K,	Λ,
Wt. %	Molarity	gm./ml.	mho cm.$^{-1}$	mho cm.^{2}
0.4324	0.0538	0.9958	0.00823	153.1
7.9779	1.0234	1.0269	0.1222	119.4
12.963	1.6940	1.0461	0.1881	111.0
14.533	1.9104	1.0523	0.2068	108.2
18.352	2.4504	1.0688	0.2528	103.2
28.572	3.9749	1.1136	0.3545	89.17
38.071	5.5065	1.1579	0.4210	76.46
47.424	7.1318	1.2038	0.4554	63.86
50.378	7.6705	1.2188	0.4590	59.84
59.457	9.4086	1.2667	0.4465	47.46
66.012	10.749	1.3035	0.4141	38.52

TABLE II

DENSITIES AND SPECIFIC AND EQUIVALENT CONDUCTANCES OF AQUEOUS SILVER NITRATE SOLUTIONS AT 35.00°C.

Concentration		d_4^{35},	K,	Λ,
Wt. %	Molarity	gm./ml.	mho cm.$^{-1}$	mho cm.^{2}
1.6612	0.0986	1.0082	0.01306	132.5
20.051	1.4023	1.1882	0.1197	85.37
24.350	1.7757	1.2389	0.1413	79.55
36.551	3.0322	1.4094	0.1983	65.41
42.849	3.8230	1.5158	0.2252	58.91
45.764	4.2306	1.5705	0.2372	56.06
51.422	5.1064	1.6874	0.2590	50.71
51.844	5.1784	1.6970	0.2606	50.32
57.194	6.1438	1.8250	0.2782	45.28
64.283	7.6633	2.0253	0.2954	38.55

Beckmann thermometer. The 35°C. thermostat showed a variation of ± 0.02°C.

Measurement of Equivalent Conductances

This has been previously described (3). Our data for specific and equivalent conductances are given in Tables I and II.

The Measurement of Relative Viscosity

It was desirable to obtain a measure of accuracy for viscosity determinations comparable to that of the conductance data. The capillary viscometer is most commonly employed in research work of this nature and has the advantage of being simple in principle and operation, but the simple Ostwald equation commonly employed with an Ostwald viscometer cannot be used for accurate work unless care is taken to design the viscometer in such a way that errors may either be accurately compensated for or made negligible. The latter alternative is much to be preferred and is the subject of a number of papers on viscometer design, most notable of which are by Willihnganz, McCluer, Fenske, and McGrew (19), and by Jones (9). It was decided that a suitable viscometer was that designed by Cannon and Fenske for nonviscous liquids (4), and two were obtained from the H. S. Martin Glass Co.

The drainage and kinetic energy corrections to the measurements were considered to be negligible by virtue of the rather narrow capillary diameter which gave an efflux time in excess of 200 sec., for all of the measurements. The surface tension correction was not allowed for in such a viscometer because the change in surface tension between the calibrating liquid, water, and an aqueous salt solution does not cause a large effect. The working volume correction was rendered negligible by the rather unique and quite sensitive method of filling the pipettes. The viscometer is inverted and the capillary arm is placed in the liquid. Suction is then applied to the wide-bore arm and the liquid is drawn to the capillary mark. This method of loading was found to be very convenient and gave quite reproducible results. Two stop watches were used which were periodically checked against station WWV, Washington, and found to be reliable for periods well in excess of the efflux times. The measurement was repeated until at least three consecutive readings were in agreement to 0.2 sec. which was the practical limit of the stop watches. The first viscometer was then transferred from one bath to the other and vice versa. It was found experimentally that the efflux time suffered no change, when a solution was heated from 25° to 35° without refilling, from the result when the filling was done at 35° as well as 25°. Each was again allowed to come to equilibrium and the procedure was repeated. The viscometer constants were checked frequently with conductance water and showed no variation over the period of this work.

All the pertinent viscosity data are tabulated for the two salts at 25.00° and 35.00° in Tables III, IV, V, and VI. The fluidities are plotted in Figs. 5 and 6 together with our previous results at 25.00°C.

The Determination of the Density

In this determination a simple Weld pycnometer was employed. Although

TABLE III

DENSITY AND VISCOSITY DATA FOR AMMONIUM NITRATE AT 25.00°C.

Molarity	Density, gm. ml.$^{-1}$		Viscosity, centipoise	Fluidity, rhes
	Exptl.	Calc.		
0.0000	0.99707	0.99707	0.8937	111.9
0.0540	0.99883	0.99883	0.8924	112.0
1.0261	1.02957	1.02957	0.8635	115.8
1.7009	1.05028	1.05029	0.8564	116.7
1.9184	1.0567	1.0569	0.8561	116.8
2.4611	1.0735	1.0734	0.8604	116.2
3.9940	1.1190	1.1187	0.9005	111.1
5.5346	1.1637	1.1636	0.9846	101.6
7.1685	1.2100	1.2101	1.1324	88.30
7.7100	1.2251	1.2252	1.1200	83.35
9.4584	1.2734	1.2734	1.5047	66.46
10.8027	1.3100	1.3098	1.8820	53.13

TABLE IV

DENSITY AND VISCOSITY DATA FOR SILVER NITRATE AT 25.00°C.

Molarity	Density, gm. ml.$^{-1}$		Viscosity, centipoise	Fluidity, rhes
	Exptl.	Calc.		
0.0000	0.99707	0.99707	0.8937	111.9
0.0989	1.0112	1.0110	0.9005	111.0
1.4077	1.1928	1.1926	0.9871	101.3
1.7830	1.2440	1.2440	1.0208	97.96
3.0458	1.4157	1.4156	1.1630	86.00
3.8399	1.5225	1.5225	1.2770	78.30
4.2526	—	1.5779	1.3427	74.48
5.1313	1.6953	1.6952	1.5031	66.52
5.2027	1.7049	1.7047	1.5198	65.80
6.1730	1.8336	—	1.7342	57.65
7.6996	2.0349	—	2.1693	46.10

TABLE V

DENSITY AND VISCOSITY DATA FOR AMMONIUM NITRATE AT 35.00°C.

Molarity	Density, gm. ml.$^{-1}$	Viscosity, centipoise	Fluidity, rhes
0.000	0.99406	0.7225	138.4
0.0538	0.99575	0.7222	138.5
1.0234	1.0269	0.7119	140.5
1.6940	1.0461	0.7114	140.5
1.9104	1.0523	0.7132	140.2
2.4505	1.0688	0.7211	138.7
3.9749	1.1136	0.7639	131.0
5.5065	1.1579	0.8427	118.7
7.1318	1.2038	0.9748	102.6
7.6705	1.2188	1.0325	96.85
9.4086	1.2667	1.2951	77.21
10.749	1.3035	1.6139	61.96

TABLE VI

DENSITY AND VISCOSITY DATA FOR SILVER NITRATE AT 35.00°C.

Molarity	Density, gm. ml.$^{-1}$	Viscosity, centipoise	Fluidity, rhes
0.0000	0.99406	0.7225	138.4
0.0986	1.0082	0.7289	137.2
1.4023	1.1882	0.8100	123.5
1.7757	1.2389	0.8385	119.3
3.0322	1.4094	0.9584	104.3
3.8230	1.5158	1.0557	94.72
4.2306	1.5705	1.1074	90.30
5.1064	1.6874	1.2401	80.64
5.1784	1.6970	1.2533	79.78
6.1438	1.8250	1.4281	70.02
7.6633	2.0253	1.7786	56.24

this instrument is not capable of the highest accuracy, it has many practical advantages over the more elaborate and time consuming methods which are commonly employed for high precision measurements (11, 18). The pycnometer had a capacity of approximately 25 ml. No advantage would have been gained by the use of a larger bottle since uncertainties due to adsorption of moisture on large surfaces become considerable beyond 30 ml. The technique employed in the use of this pycnometer was exactly that of Weissberger (17). The appropriate buoyancy corrections were made from a knowledge of the temperature, pressure, and humidity.

The empirical equation of Gucker (6) for the densities of ammonium nitrate solutions at 25.00°C. up to saturation is: $d_4^{25} = 0.997077 + 0.032628c - 9.63 \times 10^{-4}c^{3/2} - 4.73 \times 10^{-5}c^2$. This equation represents the experimental data of Adams and Gibson (1) to two parts in the fifth decimal place. The experimental densities for six ammonium nitrate solutions determined in a single day are presented in Table VII, together with values calculated from this equation.

TABLE VII

Weight % NH_4NO_3	Normality	d_4^{25}	
		Experimental	Calculated
1.4812	0.1856	1.00305	1.00305
1.7248	0.2163	1.00403	1.00404
6.2710	0.8010	1.02251	1.02249
10.048	1.3031	1.03803	1.03809
15.537	2.0599	1.06124	1.06124
24.759	3.4075	1.10167	1.10165

The density data for the determinations at 25.00°C. and 35.00°C. are contained in Tables III, IV, V, and VI. For comparative purposes Table III also contains the values calculated from Gucker's equation (6). Calculated values

for silver nitrate at 25.00°C. for concentrations up to 5 molar were also obtained from the equation of Jones and Colvin (10):

$$d_4^{25} = 0.997074 + 0.141956c - 0.002603c^{3/2}$$

These values are included in Table IV.

Apparent Molal Volume

The apparent molal volumes of ammonium nitrate solutions at 25.00°C. have been very accurately determined by Adams and Gibson (1) and by Gucker (6). The apparent molal volumes of silver nitrate at 25.00°C. have been determined by Bauer (2). The agreement of his values with ours is dependent on the agreement of the density figures. Our density data differ from their accurate results by as much as two units in the fourth decimal place and consequently the molal volume data presented in Table VIII for

TABLE VIII

THE APPARENT MOLAL VOLUMES OF NH_4NO_3 AND $AgNO_3$ SOLUTIONS AT 35.00°C.

Ammonium nitrate				Silver nitrate			
c	$\sqrt{c}$	d_4^{35}	Φ	c	$\sqrt{c}$	d_4^{35}	Φ
1.0234	1.011	1.0269[6]	48.2 ± .2	1.4023	1.184	1.1881[9]	31.6 ± .1
1.6940	1.301	1.0460[7]	49.6 ± .1	1.7757	1.332	1.2388[8]	32.2 ± .1
1.9104	1.382	1.0523[9]	49.9 ± .1	3.0322	1.741	1.4093[8]	33.22 ± .06
2.4504	1.565	1.0687[9]	49.9 ± .1	3.8230	1.955	1.5157[6]	33.73 ± .05
3.9749	1.994	1.1136[2]	50.27 ± .05	4.2306	2.057	1.5705[4]	33.93 ± .04
5.5065	2.347	1.1578[6]	50.60 ± .04	5.1064	2.259	1.6873[7]	34.32 ± .03
7.1318	2.671	1.2037[6]	50.95 ± .03	5.1784	2.276	1.6969[5]	34.36 ± .03
7.6705	2.770	1.2188[1]	51.05 ± .03	6.1438	2.479	1.8249[7]	34.85 ± .03
9.4086	3.067	1.2667[0]	51.38 ± .02	7.6633	2.768	2.0253[2]	35.53 ± .03
10.749	3.278	1.3034[9]	51.57 ± .02				

35.00°C. are quoted to only as many figures as this error justifies. The probable errors in the apparent molal volume, determined on the assumption that the 35.00°C. density figures were of comparable accuracy to those at 25.00°, were calculated and included in the table.

The Temperature Coefficients

It is commonly stated that the variation of conductance with temperature may be expressed by means of an equation, usually of the form

$$\Lambda_t/\Lambda_{25^\circ} = 1 + a(t - 25) + b(t - 25)^2 + \ldots$$

where a and b are constants to be determined.

There is no generally applicable formula for the temperature dependence of viscosity or fluidity, but it is agreed, both on empirical and theoretical grounds, that it should contain an exponential expression of the form, $e^{E/RT}$.

The proper evaluation of the coefficients of the above equation and the determination of the temperature dependence of the fluidity must be left until further data are obtained in the range between 35.00°C. and 95.0°C. The procedure followed by us (3) in the determination of "coefficients" between 25.00° and 95.0°C. was adopted. The variation of both the equivalent conductance and the fluidity between 25.00°C. and 35.00°C. was assumed to be

linear and average temperature coefficients were evaluated. No appreciable error was introduced by evaluating graphically the coefficients at concentrations somewhat removed from the experimental points. The results are presented in Table IX. The ratio of the temperature coefficient of fluidity to the

TABLE IX

TEMPERATURE COEFFICIENTS OF CONDUCTANCE AND FLUIDITY BETWEEN 25.00° AND 35.00°C.

Molarity	Ammonium nitrate			Silver nitrate		
	Coefficient of:		γ/β	Coefficient of:		γ/β
	Fluidity, γ	Conductance, β		Fluidity, γ	Conductance, β	
0.00	2.37×10^{-2}	1.86×10^{-2}	1.27	2.37×10^{-2}	1.88×10^{-2}	1.26
1.00	2.14	1.85	1.16	2.20	—	—
2.00	2.00	1.69	1.18	2.15	1.90	1.13
3.00	1.86	1.65	1.13	2.13	1.90	1.12
4.00	1.77	1.56	1.13	2.07	1.88	1.10
5.00	1.69	1.50	1.13	2.03	1.85	1.10
6.00	1.62	1.44	1.13	2.08	1.92	1.08
7.00	1.58	1.43	1.10	2.12	1.95	1.09
8.00	1.53	1.39	1.10	2.14	1.92	1.11
9.00	1.50	1.38	1.09	—	1.93	—
10.00	1.53	1.30	1.18	—	—	—

temperature coefficient of equivalent conductance is of interest and this ratio is also included.

The Saturated Solutions

These results are of special interest from the point of view of solubilities, and since they are probably not of comparable accuracy, they are not included in tables with the other solutions but are presented separately in Table X.

TABLE X

CONCENTRATION, DENSITY, CONDUCTANCE, AND FLUIDITY OF SATURATED SOLUTIONS AT 25.00° AND 35.00°C.

Salt	t,°C.	Wt. %	Lit. solubility, wt. %	d	Lit. d	Molarity	K	Λ	ϕ
NH_4NO_3	25.00	67.3	67.6	1.3174	1.3197	11.08	0.3519	31.76	50.05
	35.00	71.5	71.6	1.3384	1.3394	11.95	0.3702	30.98	48.06
$AgNO_3$	25.00	71.0	71.0	2.3019	2.3021	9.62	0.2509	26.10	33.25
	35.00	75.4	75.4	2.4530	—	10.90	0.2943	27.00	33.09

DISCUSSION OF RESULTS

Conductance

The variation of equivalent conductance with concentration at 35.00°C. is seen (Figs. 1 and 2) to be similar to that (3) at 25.00°C. The approximately linear variation at high concentrations persists although a noticeable curvature

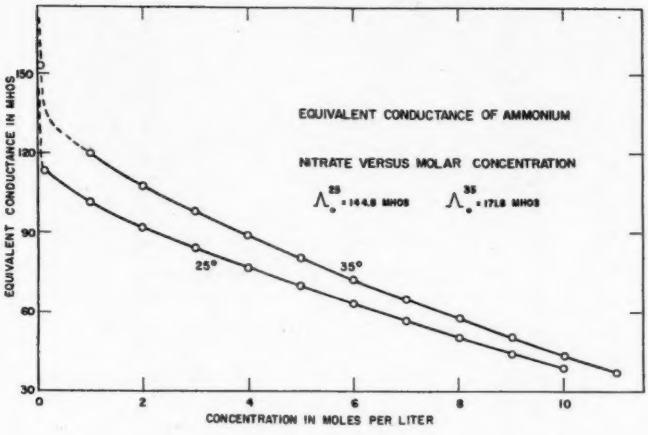

FIG. 1

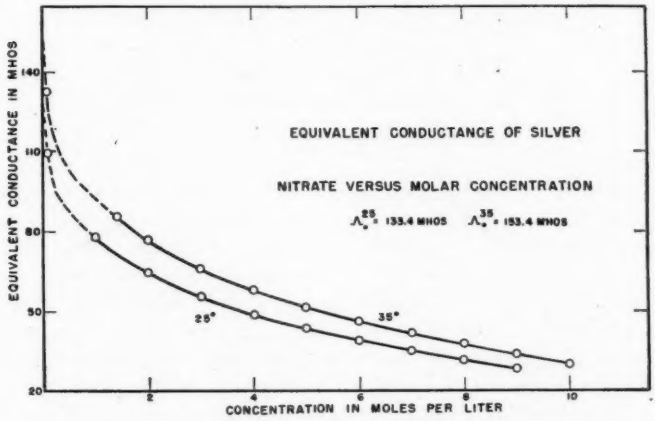

FIG. 2

may be detected on a large scale plot. The trend to increasing curvature with rising temperature is evident from the data at 95.00°C. (3) where the deviations from linearity are quite pronounced. The equivalent conductances of ammonium nitrate are numerically greater than those of silver nitrate and tend to linearity at a lower concentration. The values at infinite dilution were obtained from the published ionic conductances and their temperature coefficients and are included in Figs. 1 and 2 to demonstrate the great variation in the dilute solution range.

Figs. 3 and 4 illustrate the behavior of the specific conductance with increase of concentration. At 95.00°C. the specific conductance of a 12 molar solution is approximately the same as that of a 4 molar solution in spite of a

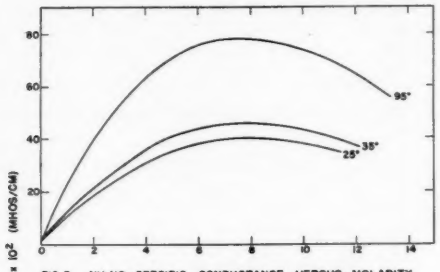

FIG. 3 NH_4NO_3 SPECIFIC CONDUCTANCE VERSUS MOLARITY

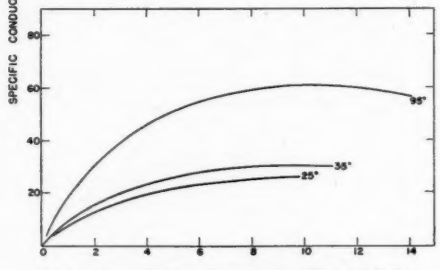

FIG. 4 $AgNO_3$ SPECIFIC CONDUCTANCE VERSUS MOLARITY

FIGS. 3 & 4

threefold increase in electrolyte concentration. This phenomenon was often noted in the early literature (16) and interpreted as the "interplay of ionization and concentration". It has only been observed infrequently in the modern literature (13) because of the lack of conductance work in the concentrated region. It seems probable that the existence of a maximum indicates the association of ions in some manner or other. In view of the present ideas on the structure of concentrated electrolytic solutions, the maximum might be explained by a more ordered lattice-like structure of the ions. In this connection it is interesting that the maxima occur at substantially the same concentration with rise in temperature, but, if anything, appear to move toward higher dilution. This behavior is not contradictory to the view that dissociation normally increases with rising temperature, since the decrease in dielectric constant, and variations in ion-solvent effects might well compensate for the increase in thermal energy. In fact it was the conclusion of early workers on independent evidence that electrolytic dissociation decreased at higher temperatures (16). Some authors would undoubtedly attribute the decrease in specific conductance to the increase in viscosity, but this does not constitute an explanation at all, especially since the variation of viscosity in no way parallels that of the conductance.

When the equivalent conductance is plotted against temperature a linear curve is obtained. This has been done for solutions of silver nitrate and of ammonium nitrate of various concentrations in Figs. 5 and 6. In order to

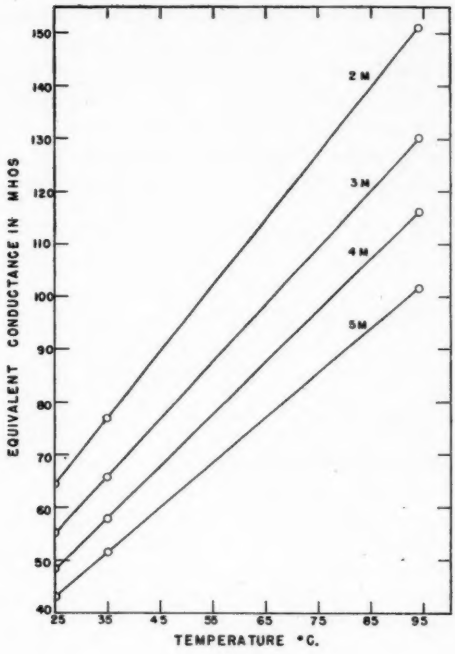
EQUIVALENT CONDUCTANCE IN MHOS
TEMPERATURE °C.
2 M
3 M
4 M
5 M

FIG. 5

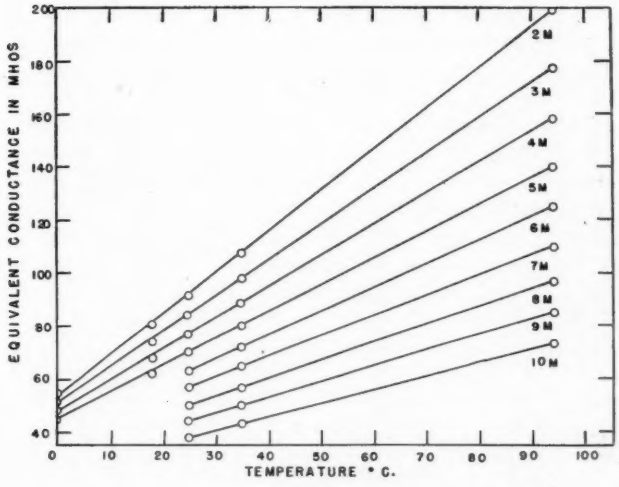
EQUIVALENT CONDUCTANCE IN MHOS
TEMPERATURE °C.
2 M
3 M
4 M
5 M
6 M
7 M
8 M
9 M
10 M

FIG. 6

construct Figs. 5 and 6 we have utilized the data of the Critical Tables taken from various sources as well as our own data. We have no explanation to offer of this linearity; that it is a coincidence is hardly likely. It certainly is not behavior that would be expected from the supposed complexity of the structure of concentrated solutions of strong electrolytes.

The fluidity data for ammonium nitrate lie very well along a smooth curve at both temperatures (Fig. 7), exhibiting a maximum between 1.7 and 2.0

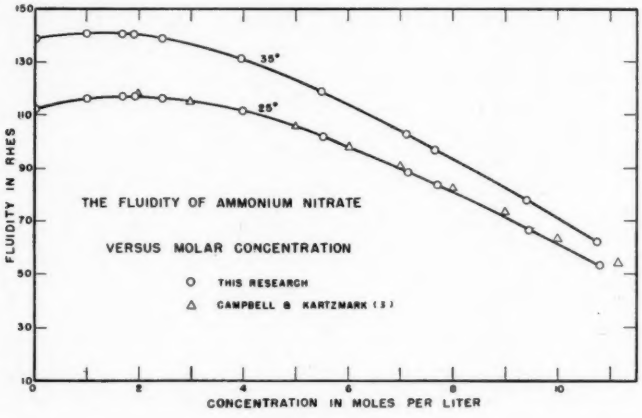

FIG. 7

molar at 25.00°C. and between 1.2 and 1.5 molar at 35.00°C. The fluidities approach linearity at the higher concentrations, the 35.00°C. curve being the more nearly linear. Our earlier data (3) for 25.00°C. are included.

The fluidity-concentration dependence of silver nitrate (Fig. 8) differs considerably from that of ammonium nitrate. The curves are S-shaped and show

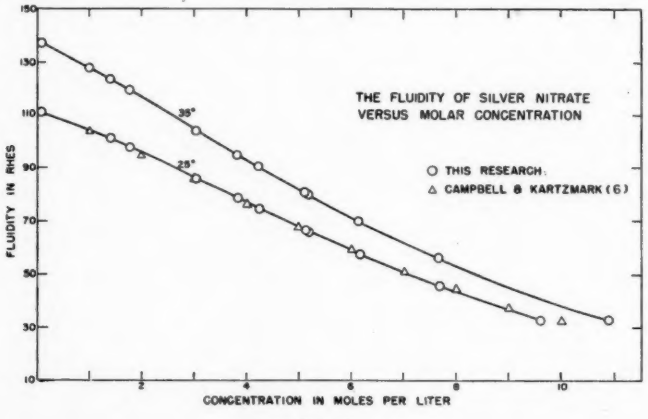

FIG. 8

a tendency to flatten out at high concentrations. Our earlier data (3) are again included.

The average coefficients of fluidity evaluated between 25.00°C. and 35.00° C. and tabulated in Table IX show a behavior roughly parallel to that of the conductance coefficients as shown by the approximate constancy of their ratios. The ratios, γ/β, are surprisingly constant considering the probable error of from 4 to 8 % in both coefficients. The fluidity coefficients are markedly different from those evaluated by us for the 25-95° range, illustrating the nonlinear dependence of fluidity on temperature. The assumption of linearity between 25.00°C. and 35.00°C. is perhaps not serious and some comparison may be made.

The apparent constancy of the ratio with concentration was pointed out by us previously (3), but an observation of perhaps greater significance is that the ratio is the same for both silver nitrate and ammonium nitrate, indicating a proportionality between the two coefficients, at least for these two salts. This shows that above 2 molar the factors which cause an increase of conductance with temperature have a proportional effect on the fluidity. The differences between the values for conductance and for fluidity are to be expected since each phenomenon proceeds by a different mechanism. Nevertheless the close relationship is clearly demonstrated, and it is probable that a mathematical treatment of the theory would contain an identical term for both conductance and fluidity.

Although the density data are quite accurate enough for use in evaluating the viscosities and the molar concentrations, they are not sufficiently so to allow the ultimate calculation of the partial molal volumes. The apparent molal volumes of ammonium and silver nitrate solutions at 35.00°C. are presented in Table VIII. Estimated errors are included on the assumption that the probable error in the densities is two parts in the fourth decimal place.

CONCLUSION

The most notable observations in this work, apart from the accumulation of experimental data, are that the plot of Λ vs. temperature is in every case a straight line, and that in the region of high concentration the (isothermal) plot of Λ vs. concentration approaches a straight line. For the former observations we have no explanation to offer. The latter observation is not new. Indeed, Hasted, Ritson, and Collie (7) point out that any equation purporting to represent the conductance behavior over the complete range of concentration would have to reduce at low concentrations to a form in which Λ is proportional to $\sqrt{c}$ and for high concentrations to a form for which Λ is proportional to c. This is mathematically possible, but there is not much point in it, unless the equation can be deduced from an acceptable model.

REFERENCES

1. ADAMS, L. H. and GIBSON, R. E. J. Am. Chem. Soc. 54: 4520. 1932.
2. BAUER, N. Dissertation. The University of Michigan Press, Ann Arbor, Mich. 1941.
3. CAMPBELL, A. N. and KARTZMARK, E. M. Can. J. Research, B, 28: 43. 1950; B, 28: 161. 1950; Can. J. Chem. 30: 128. 1952.
4. CANNON, M. J. and FENSKE, M. R. Ind. Eng. Chem. Anal. Ed. 10: 299. 1938.

5. GETMAN, F. H. J. Am. Chem. Soc. 30: 721. 1908.
6. GUCKER, F. T. J. Phys. Chem. 38: 307. 1934.
7. HASTED, J. B., RITSON, D. M., and COLLIE, C. H. J. Chem. Phys. 16: 1. 1948.
8. International critical tables. McGraw-Hill Book Company, Inc., New York. 1930.
9. JONES, G. J. Am. Chem. Soc. 60: 1691. 1938.
10. JONES, G. and COLVIN, J. H. J. Am. Chem. Soc. 62: 338. 1940.
11. MACINNES, D. A. and DAYHOFF, M. O. J. Am. Chem. Soc. 74: 1017. 1952.
12. MACINNES, D. A., SHEDLOVSKY, T., and LONGSWORTH, L. G. Chem. Revs. 13: 29. 1933.
13. MEAD, D. J. and FUOSS, R. M. J. Phys. Chem. 49: 480. 1945.
14. SCATCHARD, G. and PRENTISS, S. S. J. Am. Chem. Soc. 54: 2696. 1932.
15. SHEDLOVSKY, T. J. Am. Chem. Soc. 54: 1411. 1923.
16. TAYLOR, H. S. A treatise on physical chemistry. D. Van Nostrand Company, Inc., New York. 1925. p. 526.
17. WEISSBERGER, A. Physical methods of organic chemistry. Vol. 1, Interscience Publishers, Inc., New York. 1945.
18. WIERTHE, H. E. J. Am. Chem. Soc. 59: 2549. 1937.
19. WILLIHNGANZ, E. H., MCCLUER, W. B., FENSKE, M. R., and MCGREW, R. V. Ind. Eng. Chem. Anal. Ed. 6: 231. 1934.

PHOTOLYSIS OF MERCURY DIMETHYL[1]

By Richard E. Rebbert[2] and E. W. R. Steacie

ABSTRACT

The photolysis of mercury dimethyl was investigated over the temperature range from 125° to 250°C. The results indicate that methane is formed only by an abstraction reaction and ethane is formed only by recombination, at least under the conditions used in these experiments. It is concluded that the activation energy of the reaction

$$CH_3 + Hg(CH_3)_2 \rightarrow CH_4 + CH_2HgCH_3$$

is 10.8 ± 0.3 kcal./mole.

INTRODUCTION

An extensive investigation was recently conducted in this laboratory to determine the activation energies of a number of reactions of the type (8)

$$CH_3 + RH \rightarrow CH_4 + R.$$

The source of the methyl radicals in all this work was the photolysis of acetone. In order to establish these results with more certainty, it was thought profitable to repeat some of these experiments using another source of methyl radicals. For this purpose, mercury dimethyl was chosen. However, before it could be used as a source of methyl radicals, some aspects of its own photolysis had to be more fully investigated. In particular it was necessary to establish that the ethane came only from the recombination of methyl radicals and not from a reaction such as

$$CH_3 + Hg(CH_3)_2 \rightarrow C_2H_6 + Hg + CH_3.$$

Although mercury dimethyl is an excellent source of methyl radicals, it is not quite as useful as acetone for two reasons. First, it begins to decompose thermally around 250°C. which limits the temperature range over which it can be used. Secondly, its vapor pressure is only 6 cm. at room temperature which limits the range over which the pressure may be varied conveniently. However, outside of these inconveniences, a very good parallelism can be drawn between the photolysis of mercury dimethyl and acetone. Both give a very good Arrhenius plot for $k_1/k_2^{\frac{1}{2}}$ from 125°C. to over 250°C., where k_1 is the rate constant for the abstraction reaction and k_2 is the rate constant for the recombination of methyl radicals. However, for both acetone and mercury dimethyl there seems to be curvature in the Arrhenius plot below 125°C. In both cases, the ratio $k_1/k_2^{\frac{1}{2}}$ is essentially independent of the light intensity over more than a twentyfold variation, and both ratios are only very slightly pressure dependent. There is a small increase of $k_1/k_2^{\frac{1}{2}}$ with a decrease of pressure. This may be due to a partial third body restriction for the recombination of methyl radicals. Further work is being done in this laboratory in the case of acetone to check this point.

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Contribution from the Division of Pure Chemistry, National Research Council, Ottawa, Canada. Issued as N.R.C. No. 2999.
[2] *National Research Council of Canada Postdoctorate Fellow, 1951-1953.*

EXPERIMENTAL

Apparatus

The light source was an Hanovia S-500 medium pressure arc. It was turned on about one hour before each run in order for it to reach constant intensity. A nearly parallel beam of light was produced by a system of two quartz lenses and two stops. This beam almost filled the reaction cell.

The quartz reaction cell was 10 cm. long and 5 cm. in diameter with a volume of 179.5 cc. This was the volume used in all calculations. The cell was placed in an aluminum block furnace which was twice the length of the cell. The over-all temperature was manually controlled to better than $\pm$ 1.0°C. during each run. The temperature was measured by means of three copper-constantan thermocouples placed in the middle and at either end of the cell.

At various times a chlorine gas filter and a Corning 7-54 or 986 filter were used. Also relative intensities could be determined by means of a R.C.A. 935 photoelectric vacuum cell in conjunction with a battery of 250 volts and a galvanometer.

The remaining apparatus consisted of storage vessels, a mercury manometer, McLeod gauge, and analytical system. The cell and mercury dimethyl storage vessel were separated from the rest of the apparatus by means of mercury cutoffs. The analytical system consisted of a LeRoy (4) still and a combination Toepler pump and gas burette. Later, another LeRoy still and a small mercury diffusion pump were added to facilitate the separation of the gases.

Material

The mercury dimethyl was obtained from the Delta Chemical Works. However, since it contained appreciable quantities of ether, it was necessary to fractionate it. Before fractionation, the vapor pressure at 0°C. was about 20 mm. Afterwards it was 17.7 mm. at 0°C. and 0.015 mm. at $-$ 78°C. (acetone–dry ice mixture). The value reported in the literature is 17.4 mm. at 0°C. and 0.0145 mm. at $-$ 80°C. (7). Its purity was then checked on the mass spectrometer and it was found to contain 0.11% ether.

RESULTS

In Tables I, II, and III are given the results of the runs performed to determine the activation energy of the reaction of methyl radicals with mercury dimethyl, the effect of variation of light intensity, and the effect of variation of concentration. Table IV gives the amount of photochemical decomposition of mercury dimethyl calculated for the same amount of absorbed light and corrected at the higher temperatures for any thermal reaction. It is seen to be approximately constant over the temperature range from 26°C. to 239°C., i.e. the quantum yield does not vary appreciably over this range of temperature.

We also found that approximately 38% of the incident light (between 2300-3000 Å) was absorbed by mercury dimethyl at a pressure of 40 mm. (at 125°C.) in a reaction cell 10 cm. long. However, this increased to better than 60% at a pressure of 52 mm. (at 240°C.). A chlorine gas filter and a Corning

7-54 or 986 filter were used to isolate the region between 2300-3000 Å.

In addition to methane and ethane, small quantities of ethylene, propane, and propylene were reported in some of the runs in which analyses were made with a mass spectrometer. However, correcting for all these gases did not change the $k_1/k_2^{\frac{1}{2}}$ ratio by more than the experimental error in the gas analysis.

TABLE I

THE PHOTOLYSIS OF MERCURY DIMETHYL

Temp. (°K.)	Pressure of $Hg(CH_3)_2$ (mm.)	Time (sec.)	Products (micromoles)		$k_1/k_2^{\frac{1}{2}} \times 10^{13}$
			CH_4	C_2H_6	
Low intensity runs†					
373	37.7	16,200	0.20	5.12	0.42
398	39.9	13,500	0.40	4.96	0.93
398	39.2	18,000	0.56	5.37	1.1
413	40.8	10,800	0.55	4.21	1.5
422	42.3	10,800	0.79	4.49	2.1
423	42.2	14,400	1.00	4.73	2.3
439	44.5	9,000	1.38	6.06	3.5
448	45.0	9,060	1.43	4.26	4.3
462	46.3	14,400	3.99	8.94	6.6
463	46.4	7,200	1.73	3.42	6.6
473	47.6	7,200	2.50	3.97	8.9
481	48.8	7,200	3.59	5.95	10.3
493	49.7	7,200	4.18	4.29	14.2
513	51.8	5,400	5.07	3.49	21.9
High intensity runs††					
443	44.0	1,800	0.89	9.92	4.0
449	44.7	1,800	1.00	9.78	4.6
472	47.8	1,200	1.31	7.24	8.3
473	47.5	1,800	2.01	10.71	8.7
498	50.5	1,200	2.36	7.42	14.8
504	51.0	1,800	4.31	11.30	19.5
525	52.7	900	3.42	5.85	28.1

†*The low intensity runs were performed with a chlorine gas filter and a Corning 7-54 filter.*
††*The high intensity runs were performed without any filters.*

TABLE II

THE EFFECT OF VARIATION OF LIGHT INTENSITY IN THE PHOTOLYSIS OF MERCURY DIMETHYL
All runs performed at 439°K.

$Hg(CH_3)_2$ pressure (mm.)	Time (sec.)	Products (micromoles)		Relative* intensity	$k_1/k_2^{\frac{1}{2}} \times 10^{13}$
		CH_4	C_2H_6		
44.0	1,800	0.87	13.03	21.3	3.4
45.3	900	0.44	6.33	20.8	3.4
47.3	3,600	0.90	5.73	4.90	3.5
44.5	9,000	1.38	6.06	2.14	3.5
43.9	16,200	1.67	4.86	1.00	3.5

**The relative light intensity was calculated on the amount of products formed in unit time.*

TABLE III

THE EFFECT OF VARIATION OF CONCENTRATION IN THE PHOTOLYSIS OF MERCURY DIMETHYL
All runs performed at 439°K.

$Hg(CH_3)_2$ pressure (mm.)	Time (sec.)	Products (micromoles)		$k_1/k_2^{\frac{1}{2}} \times 10^{13}$
		CH_4	C_2H_6	
47.3	3,600	0.90	5.73	3.5
44.5	9,000	1.38	6.06	3.5
24.5	3,600	0.43	3.82	3.9
12.9	10,800	0.44	3.59	4.6
6.4	12,600	0.18	2.23	4.5

TABLE IV

RELATIVE QUANTUM YIELDS

Pressure of $Hg(CH_3)_2$ (mm.)	Temp. (°C.)	$Hg(CH_3)_2$ decomposed ($\frac{1}{2}$ CH_4 + C_2H_6) (micromoles/hr.)	Light absorption (%)	$Hg(CH_3)_2$ decomposed at constant absorbed intensity (29.5%)	Relative Q.Y. (± 0.1)
29.2	26	1.44	17.8	2.39	0.92
36.7	99	2.60	29.5	2.60	1.00
41.8	141	3.28	40.2	2.41	0.93
47.3	198	4.95	52.5	2.78	1.07
51.3	239	6.77	64.5	3.10	1.20

In the subsequent calculations, therefore, the figures used are the ones obtained by the gas analysis since only a few analyses were made with the mass spectrometer.

Finally, it may be noted that in the few runs checked with the photoelectric cell, there was an increase of absorption as more mercury dimethyl was decomposed. This effect occurred only at the high temperatures where an appreciable amount of methane was formed. This increase of absorption must be due to the formation of some product which absorbs even more strongly than the mercury dimethyl in the region 2300-3000 Å. The most probable products are $C_2H_5HgCH_3$ and $(CH_3HgCH_2)_2$.

DISCUSSION

In the temperature range from 125°C. to 250°C., the main steps in the photolysis of mercury dimethyl may be described by the following equations:

$$Hg(CH_3)_2 + h\nu \rightarrow Hg + 2CH_3 \quad [0]$$

$$CH_3 + Hg(CH_3)_2 \rightarrow CH_4 + CH_2HgCH_3 \quad [1]$$

$$2CH_3 \rightarrow C_2H_6 \quad [2]$$

$$CH_3 + CH_2HgCH_3 \rightarrow C_2H_5HgCH_3 \quad [3]$$

$$2CH_2HgCH_3 \rightarrow (CH_3HgCH_2)_2 \quad [4]$$

We exclude a reaction as

$$CH_2HgCH_3 \rightarrow CH_2 + Hg + CH_3 \quad [5]$$

since such a reaction would yield chains which would increase the amount of mercury dimethyl decomposed as the temperature is increased, and as seen from Table IV this is not the case.

Moreover, Polanyi (6) has postulated that the CH_2HgCH_3 radical is very stable even at temperatures over 500°C. This conclusion is based on the thermal decomposition of mercury dimethyl in a flow system in the presence of various other gases. The rate constant, which was determined by measuring the amount of mercury and also the amount of methane and ethane formed, is found to be the same in the presence or absence of toluene. With the addition of toluene, methane is also formed from the following reaction:

$$CH_3 + C_6H_5CH_3 \rightarrow CH_4 + C_6H_5CH_2 \quad [6]$$

in addition to reactions [1] and [2]. Since this lowers the steady state concentration of methyl radicals, less methane is formed from reaction [1] in the presence of toluene and consequently less CH_2HgCH_3 radicals are formed with toluene than without it. Now if the CH_2HgCH_3 radicals decomposed, a higher rate constant would be obtained without toluene than with it. However, this is contrary to what was found, and hence he concluded that the CH_2HgCH_3 radical is stable.

We also exclude the reaction

$$CH_3 + CH_3HgCH_3 \rightarrow C_2H_6 + Hg + CH_3 \quad [7]$$

since this also would lead to a chain reaction. Reaction [7] was suggested in previous work to account for the slight increase of ethane with an increase of temperature. However, this effect can easily be accounted for by the increasing amount of light absorption with temperature. The light absorption doubles from 100°C. to 250°C. In agreement with this, Professor Noyes (5) has told us that in some recent work at his laboratory the quantum yield of mercury dimethyl was approximately 1.0 at 25°C. and also at 200°C. These results certainly indicate that reaction [7] cannot be occurring to any extent under our conditions. Reaction [7] has also been excluded in the pyrolysis of mercury dimethyl by Polanyi (6) and also by Ingold and Lossing (3) who have followed the production of radicals in the reaction by means of a mass spectrometer. Gomer and Noyes (2) included a reaction of the type of reaction [7] proceeding through an intermediate complex. The evidence for this reaction was a falling off in the slope of the plot of $R_{C_2H_6}/R_{CH_4}$ versus R_{CH_4} at very high intensities, where $R_{C_2H_6}$ and R_{CH_4} are the rates of formation of ethane and methane respectively. It may be that at such high intensities reaction [7] does occur to some extent, but it is certainly not important under our conditions.

Reactions [3] and [4] are included to remove the CH_3HgCH_2 radicals formed in reaction [1]. No attempt was made to isolate these products. The only supporting evidence is the increase of absorption with time.

From the above mechanism, we have

$$R_{CH_4} = k_1 [CH_3] [Hg(CH_3)_2] \quad \text{and}$$
$$R_{C_2H_6} = k_2 [CH_3]^2.$$

Hence,

$$\frac{k_1}{k_2^{\frac{1}{2}}} = \frac{R_{CH_4}}{R_{C_2H_6}^{\frac{1}{2}}} [Hg(CH_3)_2]$$

$$= \frac{P_1 Z_1}{P_2^{\frac{1}{2}} Z_2^{\frac{1}{2}}} e^{-(E_1 - \frac{1}{2}E_2)/RT},$$

where E_1 and E_2 are the activation energies of reaction [1] and [2]; Z_1 and Z_2, the number of collisions occurring between methyl radicals with mercury dimethyl and methyl radicals with each other at unit concentration in unit time; and P_1 and P_2 are the steric factors for the two reactions.

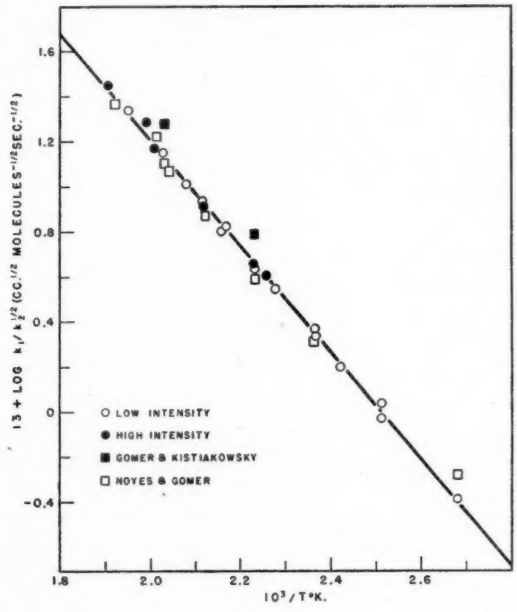

FIG. 1

In Fig. 1 the logarithm of $k_1/k_2^{\frac{1}{2}}$ is plotted against the reciprocal of the absolute temperature. All rate constants are in molecules, cc., and sec. The best line through all points has been found by the method of least squares to be

$$\log (k_1/k_2^{\frac{1}{2}}) = -7.07 - (2360/T).$$

The slope of this line gives a value of 10.8 kcal. per mole for $E_1 - \frac{1}{2}E_2$. Also in Fig. 1 are plotted the values of $k_1/k_2^{\frac{1}{2}}$ determined by Gomer and Noyes (2) and by Gomer and Kistiakowsky (1), but recalculated according to the above method. The results of Gomer and Noyes are in excellent agreement with our own, even though they were performed at 20.0 mm. pressure (at 300°K.),

while ours were done at 30.0 mm. pressure (at 300°K.). The results of Gomer and Kistiakowsky are also seen to be in fair agreement.

REFERENCES

1. GOMER, R. and KISTIAKOWSKY, G. B. J. Chem. Phys. 19: 85. 1951.
2. GOMER, R. and NOYES, W. A., JR. J. Am. Chem. Soc. 71: 3390. 1949.
3. INGOLD, K. U. and LOSSING, F. P. Private communication.
4. LEROY, D. J. Can. J. Research, B, 28: 492. 1950.
5. NOYES, W. A., JR. Private communication.
6. POLANYI, J. C. Ph. D. Thesis. Manchester. 1952.
7. RATMAN, F. J. Applied Chem. (U.S.S.R.) 9: 593. 1936.
8. TROTMAN-DICKENSON, A. F. and STEACIE, E. W. R. J. Chem. Phys. 18: 1097. 1950; TROTMAN-DICKENSON, A. F., BIRCHARD, J. R., and STEACIE, E. W. R. J. Chem. Phys. 19: 163. 1951;
TROTMAN-DICKENSON, A. F. and STEACIE, E. W. R. J. Chem. Phys. 19: 329. 1951.

THE STABILITY OF SOME COMPLEXES OF TRIVALENT COPPER[1]

By M. W. Lister

ABSTRACT

New methods are given for the preparation of sodium copper (111) tellurate, $Na_9Cu(TeO_6)_2.16H_2O$, and sodium copper (111) periodate, $Na_7Cu(IO_6)_2.20H_2O$, previously reported by Malatesta. Additional analytical evidence is presented that these are really compounds of trivalent copper. The dissociation of the ions in alkaline aqueous solution was examined through the ability of the uncomplexed copper to catalyze the decomposition of sodium hypochlorite. Evidence is presented that the uncomplexed copper ion is $Cu(OH)_4^-$, and this gives both a 1-1 and a 1-2 complex with both tellurate and periodate. The 1-2 complexes appear to be $Cu(HTeO_6)_2^{-7}$ and $Cu(IO_6)_2^{-7}$ respectively; the 1-1 complexes are less stable. The equilibrium constants for the reversible dissociation of these ions into their simpler constituents in aqueous solution at 40°C. are as follows: tellurate, 1-1 complex $K_1 = 1.8 \times 10^{-6}$; 1-2 complex $K_2 = 1.1 \times 10^{-11}$; periodate, 1-1 complex $K_1 = 3.4 \times 10^{-5}$; 1-2 complex $K_2 = 8.0 \times 10^{-11}$. The smaller the constant the more stable the complex ion. In the case of the tellurate complex K_2 is proportional to the square of the hydroxide ion concentration and these values are for 0.400 *M* sodium hydroxide; with periodate K_2 is independent of the hydroxide concentration. Experiments at various temperatures give 20 kcal. as the heat of the reaction forming the 1-2 tellurate complex from the simple ions, and 7½ kcal. for the 1-2 periodate complex. The stannate, stibnate, and selenate ions showed no signs of forming analogous compounds.

Reports of trivalent copper compounds have appeared at various times for at least a hundred years (e.g. References 2, 4, 6, and 9), but the instability of the substances obtained often made it impossible to prepare samples of reproducible composition, or to purify an impure sample. Hence there was always some doubt about the valency of the copper, and it was not really proved that the oxidizing power of the substances could not be ascribed to some other chemical grouping, such as peroxide. However Malatesta (7) prepared a number of crystallizable compounds by complexing the copper with telluric or periodic acids, and it was evident that these compounds were much more stable than those previously obtained. Their analyses agreed well with trivalent copper compounds, and they were diamagnetic which makes it certain that the copper is in an odd valency state. To oxidize the copper Malatesta used persulphate or electrolytic oxidation, which admittedly might give rise to peroxides, but the diamagnetism would seem to dispose of this possibility.

The present work describes the preparation of what are substantially the same compounds by oxidation with sodium hypochlorite. This is a further argument against supposing peroxide to be present, because this is rapidly decomposed by hypochlorite. It was also found that this method of preparation allowed information to be obtained about the stability of the complex ions in solution, as well as giving evidence for their formulae. This is based on the fact, reported by Chirnoaga (3) and checked in the present work, that copper catalyzes the decomposition of hypochlorite, and that the rate of decomposition is directly proportional to the amount of copper present. This observation

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suggested the idea that it might be possible to measure the amount of uncomplexed copper present by measuring the rate of catalytic decomposition of hypochlorite. The results obtained were consistent with this supposition; and, accepting this, it then became possible to determine the formulae of the complex ions in solution, and to measure the equilibrium constants for their formation from their constituent ions; by operating at several temperatures the heats of these reactions were obtained. A number of somewhat similar anions were also examined for complexing properties with copper, but no stable complex was found.

EXPERIMENTAL

1. Preparation of Sodium Copper (111) Periodate

Various methods of preparing this compound were tried; of these the following is probably the most satisfactory.

The hypochlorite solution was made by passing chlorine into sodium hydroxide solution in the usual way: it was about 1.5 *M* in sodium hypochlorite and 0.4 *M* in sodium hydroxide. Twelve grams of sodium hydroxide was added to 160 ml. of this solution, and after this had dissolved a solution of 2.55 gm. of copper (11) chloride dihydrate dissolved in 80 ml. of water was added. This gives an immediate precipitate of the blue $Cu(OH)_2$ which turns black in a few seconds to give what is presumably either Cu_2O_3 or $Cu(OH)_3$. This is appreciably soluble in sodium hydroxide solution. To this mixture 8.8 gm. of sodium periodate, $Na_2H_3IO_6$, was added dissolved in 60 ml. of 0.6 *M* sulphuric acid. Most of the copper dissolved and the solution was rapidly filtered. On standing a brown powder separated. This was filtered on sintered glass, washed with cold dilute sodium hydroxide solution, and dried over calcium chloride. This brown product analyzed as $Na_7Cu(IO_6)_2.16H_2O$; as the following results show.

$Na_7Cu(IO_6)_2.16H_2O$ calc.: Na 16.8%, Cu 6.6%, IO_6 46.5%, H_2O 30.0%;
obs.: Na 16.8%, Cu 7.4%, IO_6 46.8%, H_2O 30.3%.

The analysis was carried out as follows. For sodium, a weighed sample was reduced with sulphur dioxide, copper (I) iodide was filtered off, and the filtrate was evaporated with added sulphuric acid and finally ignited with ammonium carbonate, and the resulting sodium sulphate weighed. The copper was determined on another sample by weighing as copper (I) iodide. The periodate was determined by dissolving a weighed sample in dilute sulphuric acid, adding potassium iodide, and titrating the iodine formed with thiosulphate. The water was found by the loss of weight at 105°C.

The valency of the copper was checked by finding the oxidation equivalent weight of the substance (i) by adding a weighed sample to acidified potassium iodide solution; and (ii) by adding a weighed sample to dilute sulphuric acid (when oxygen is evolved and Cu^{++} formed), then adding potassium iodide. In both cases the iodine liberated was titrated with thiosulphate. In the first case the equivalent weight is the molecular weight divided by 18; in the second case by 17. The results were:

(i) Equivalent weight, calc.: 958.6/18 = 53.26;
obs.: 53.42;

(ii) Equivalent weight, calc.: 958.6/17 = 56.39;
obs.: 56.08.

This was checked by making up a solution of this compound in dilute alkali and determining its oxidizing normality in the two ways given above, with the results:

(i) 0.0828 *N* Ratio 1.056; calc. 18/17 = 1.059;
(ii) 0.0784 *N*.

This compound is thus very similar to the $Na_7Cu(IO_6)_2.12H_2O$ reported by Malatesta (7).

2. Preparation of Sodium Copper (111) Tellurate

One gram of copper (11) chloride dihydrate was dissolved in 30 ml. of water and added to 60 ml. of warm (50°C.) sodium hypochlorite solution containing an additional 5 gm. of sodium hydroxide. After stirring, 3.4 gm. of sodium tellurate, $Na_2H_4TeO_6$, was added, dissolved in a minimum amount of 0.4 *M* sulphuric acid. The solution was well stirred and warmed to 75°C., and rapidly filtered from any undissolved copper oxide. On cooling the filtrate, brown crystals separated. These were filtered, washed with dilute sodium hydroxide, and dried. They analyzed as follows:

$Na_9Cu(TeO_6)_2.20H_2O$; calc.: Na 19.2%, Cu 5.9%, Te 23.7%, H_2O 33.4%;
obs.: Na 19.0%, Cu 6.0%, Te 23.0%, H_2O 33.9%.

The sodium was estimated by removing the tellurium from a weighed sample by saturating with sulphur dioxide and filtering, then the copper (after sulphur dioxide was boiled off) by saturating with hydrogen sulphide and filtering, and evaporation of the filtrate with sulphuric acid, as before: the resulting sodium sulphate was weighed. The copper was determined by adding a little potassium iodide to a sample dissolved in dilute sulphuric acid; the iodine formed was removed by titration with thiosulphate; then the copper (1) iodide was filtered and weighed. The tellurium was precipitated by sulphur dioxide and weighed. The water loss appeared to go in two stages: on drying at 95°C. between 15 and 16 H_2O were lost; on heating to 150°C. the loss was as reported above.

The oxidation equivalent weight was found, as before, either by (i) adding the salt to acidified potassium iodide solution, or (ii) adding the salt to dilute sulphuric acid, and later adding potassium iodide. The results were:

(i) Equivalent weight: calc.: 1078/2 = 539;
obs.: 535;
(ii) Equivalent weight: calc.: 1078;
obs.: 1080.

In the first case Cu(111) goes to Cu(1); in the second Cu(11) goes to Cu(1).

Both of these compounds lose oxygen on acidification, giving the ordinary blue copper ion. It was noticed that when dilute sulphuric or nitric acid (2-3 *M*) was added to either of the solid salts, a scarlet color was briefly visible near the surface of the salt. It seems possible that this is the color of the Cu^{+++} ion; this color rapidly disappeared, and the half life of this ion in acid solution at room temperature can only be a few seconds.

Another preparation of the complex periodate, crystallized at a higher temperature gave analytical results agreeing with the compound $Na_7Cu(IO_6)_2.12H_2O$, reported by Malatesta. This gave 7.0% copper (calc. 7.2%); and equivalent weights (i) on adding to potassium iodide solution: 49.3 (calc. 49.2); and (ii) on adding to acid followed later by potassium iodide: 51.4 (calc. 52.1).

3. Measurements in Solution

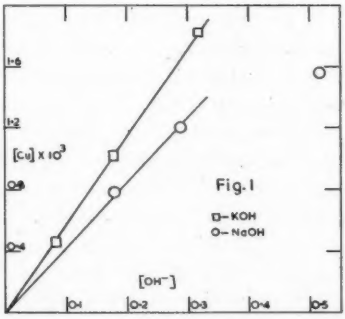
The solubility of copper in alkaline hypochlorite solutions was measured with a view to obtaining information on the ion present before addition of periodate or tellurate. Dilute aqueous copper chloride was added to the sodium hypochlorite solution until a permanent precipitate was obtained, the solution was filtered, and the copper concentration measured. This was done either by (i) measurement of the rate of oxygen evolution; or (ii) by gravimetric analysis: hydrogen peroxide decomposes hypochlorite, and precipitates any copper present (probably as CuO); this was filtered, washed, and dissolved in dilute sulphuric acid; the copper was converted to cuprous iodide and weighed as such on a porous glass filter. The estimation of copper from the rate of oxygen evolution is explained later. The results were:

(i) Solution in 1.022 *M* sodium hypochlorite. This solution also contained sodium chloride and some sodium chlorate, and the ionic strength before the addition of the copper was 3.7. The alkali concentrations were altered by adding concentrated hydrochloric acid from a burette with the tip dipping well into the stirred solution (before addition of copper).

[NaOH]:	0.179	0.286	0.518 *M*
[Cu]:	0.79	1.20	$1.56 \times 10^{-3} M$

(ii) Solution in 0.61 *M* potassium hypochlorite; ionic strength 1.5.

[KOH]:	0.082	0.177	0.319 *M*
[Cu]:	0.46	1.03	$1.83 \times 10^{-3} M$



The results are plotted in Fig. 1. At the lower concentrations there is a rough proportionality between the copper and hydroxide concentrations, this suggests that the copper ion in these solutions is $Cu(OH)_4^-$, formed by

$$Cu(OH)_3 \text{ (solid)} + OH^- \longrightarrow Cu(OH)_4^-.$$

This would be similar to the zincate ion $Zn(OH)_4^{--}$. However it is surprising that copper, with a lower charge on the ion, is less soluble in hydroxide solutions than zinc. These experiments do not altogether exclude the possibility that copper trihydroxide is present as a colloidal dispersion peptized by hydroxide ions. In support of this we have the somewhat erratic point at higher concentration. It was also observed that if barium chloride was added to the hypochlorite, and any barium carbonate formed was filtered off, then copper chloride added to the solution in small amounts gave no precipitate; but on now adding a little sodium carbonate there was formed a red or pink precipitate which contained virtually all the copper. This again could be a case of coprecipitation of barium cuprate(III)—Krüger (6) describes a red precipitate $BaCu_2O_4$, or perhaps $Ba(Cu(OH)_4)_2$—on barium carbonate, but it is a surprisingly complete precipitation. On the whole it seems fair to conclude that at low concentrations, and we shall be dealing with very low concentrations of uncomplexed copper in the periodate or tellurate solutions, the copper is present as $Cu(OH)_4^-$, but that this is not certain at high concentrations.

4. Apparatus and Reagents for the Measurement of Equilibrium Constants

The general method used in these experiments was to add a known amount of copper chloride to a known volume of sodium hypochlorite solution, and then to measure the rate of oxygen evolution at a definite temperature. Known amounts of sodium periodate or tellurate were now added, and the rate again measured after time was allowed for it to come to a steady value.

Apparatus

The solution was contained in a 1 liter flask fitted with a mercury sealed stirrer and connected through a capillary to a water jacketed gas burette. The flask had a side arm for addition of reagents or removal of samples for analysis. It was immersed in a thermostat regulated to $\pm$ 0.05°C.

Reagents

Sodium hypochlorite.—This was prepared by passing chlorine into sodium hydroxide solution, so sodium chloride was also present. The initial composition of this stock solution was 1.69 *M* sodium hypochlorite, 1.93 *M* sodium chloride, 0.022 *M* sodium chlorite, 0.029 *M* sodium chlorate, 0.400 *M* sodium hydroxide, and 0.030 *M* sodium carbonate: the ionic strength was therefore 4.19. During a run, and also slowly on storage, some of the hypochlorite was converted to chloride and chlorate, but this does not change the ionic strength. It is difficult to be certain that such a solution does not itself contain traces of copper which might affect the later results. However its rate of oxygen evolution was only that which could have been produced by $1.0 \times 10^{-6} M$ copper, so this is an upper limit to the amount of copper which could be present as an impurity. Furthermore this rate of evolution persisted in the presence of considerable amounts of periodate, which makes it very probable that this rate is due to the uncatalyzed decomposition of sodium hypochlorite. The observed rates were corrected for this uncatalyzed decomposition, when they were used to calculate the amount of uncomplexed copper present.

Copper chloride.—This was a reagent grade, recrystallized from water. Its solutions were made up by direct weighing, though this was always checked by titrating the copper in the solution iodometrically.

Sodium periodate.—This was made by heating potassium iodide with excess alkaline sodium hypochlorite. On cooling, sodium periodate crystallizes out. The crystals were washed and dried, and analyzed as $Na_2H_3IO_6$. Potassium periodate was also used, and was a reagent grade product analyzing as KIO_4.

Tellurium dioxide.—A reagent grade of tellurium dioxide was used, dissolved in dilute potassium hydroxide solution. The tellurium content was checked by precipitation as tellurium (by sulphur dioxide), and weighing. It will be noticed that the tellurium was added as tellurite, not tellurate, but it is oxidized by the hypochlorite. This reaction was used to prepare sodium tellurate, when making sodium copper (111) tellurate.

5. Rate of Reaction Catalyzed by Copper

It was first necessary to establish the kinetics of the decomposition by copper in order to be able later to deduce the concentration of the uncomplexed copper from the observed rates of reaction. Chirnoaga (3) measured the rate of this decomposition and found it to be the first order with respect to copper and hypochlorite. However his solutions differed considerably from the present ones, being more dilute in hypochlorite and much more concentrated in copper; in fact much of his copper must have been present as a suspension of copper hydroxide.

In the following runs known amounts of copper chloride were added to the stock hypochlorite, and the mixture maintained at a constant temperature; at intervals samples were analyzed for hypochlorite and the rate of oxygen evolution was measured. It was necessary to allow a considerable time to elapse between adding copper chloride and measuring the rate of gas evolution, as the concentration of gas in solution changes with its rate of evolution, thus leading to an apparent induction period. The following results show the rate to be the first order with respect to copper. In that case the actual rate of gas evolution will be proportional to the weight of copper regardless of the total volume of solution. Accordingly in column 5 of Table I the rate of oxygen evolution (in ml./min.) divided by the number of gram molecules of copper present is given. All the runs in Table I were at 50°C.

In Fig. 2 the column, rate/Cu, is plotted against the hypochlorite concentration. It is seen that by doing this these runs are superimposed, proving that the reaction is first order with respect to copper. However the dependence on hypochlorite is less simple, since the points lie on a line that does not extrapolate to the origin; in fact we can write:

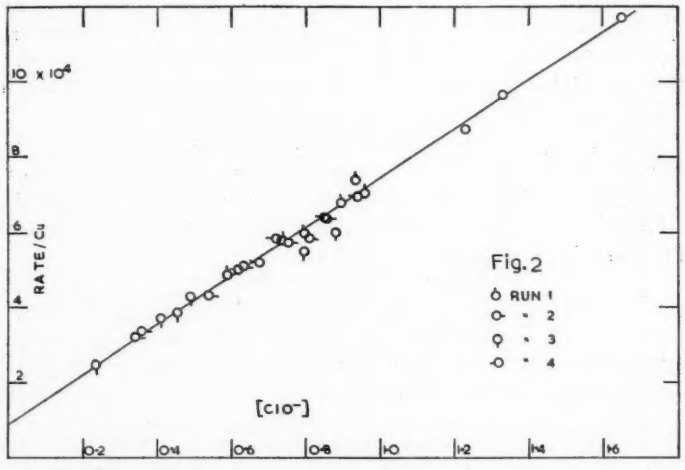
$$\text{Rate} = [\text{Cu}].\{a + b\,[\text{ClO}^-]\}$$

where a and b are constants. This would indicate that two reactions are present: (i) a preponderant reaction similar to that found by Chirnoaga which is first order with respect to copper and hypochlorite; and (ii) a less important reaction independent of the hypochlorite, which is presumably a spontaneous decomposition of the oxidized copper. The values of the constants at 50°C. are

$$\text{Rate} = [\text{Cu}].\{0.9 + 6.5\,[\text{ClO}^-]\} \times 10^4$$

TABLE I

Run	Copper added	Gas rate, ml. NTP/min.	Mean [ClO^-]	Rate/Cu
1	0.5 ml. of 0.0300 *M* $CuCl_2$	1.059	0.956 *M*	7.06×10^4
		1.110	0.935	7.40
		1.016	0.895	6.77
	Total vol. 799 ml.	0.899	0.794	5.99
		0.872	0.738	5.81
		0.727	0.589	4.85
2	4 ml. of 0.00295 *M*	0.754	0.854	6.39
	6 ml. of 0.00295 *M*	1.040	0.811	5.87
	8 ml. of 0.00295 *M*	1.362	0.754	5.77
	10 ml. of 0.00295 *M*	1.507	0.635	5.11
	12 ml. of 0.00295 *M*	1.533	0.539	4.33
	14 ml. of 0.00295 *M*	1.390	0.370	3.37
	16 ml. of 0.00295 *M* Total vol. 850 ml.	1.538	0.344	3.26
3	2 ml. of 0.0300 *M*	3.593	0.887	5.99
		3.300	0.797	5.50
	Total vol. 810 ml.	2.597	0.489	4.33
		2.305	0.459	3.84
		2.221	0.414	3.70
		1.545	0.231	2.58
4	2 ml. of 0.00279 *M*	0.388	0.940	6.95
	6 ml. of 0.00279 *M*	1.068	0.855	6.38
	10 ml. of 0.00279 *M*	1.636	0.729	5.86
	14 ml. of 0.00279 *M*	2.039	0.675	5.22
	18 ml. of 0.00279 *M* Total vol. 800 ml.	2.526	0.625	5.03
5	2 ml. of 0.0277 *M* Total vol. 512 ml.	6.51	1.65	11.78
6	1 ml. of 0.0277 *M* Total vol. 509 ml.	2.43	1.23	8.77
7	1 ml. of 0.0277 *M* Total vol. 538 ml.	2.68	1.33	9.67



where the rate is expressed in gm-atoms of oxygen liberated per minute per liter of solution. The uncatalyzed rate only makes a very small contribution to these total rates, being between 0.02 and 0.04 ml./min. There is also a slow conversion of hypochlorite to chlorate which is independent of the oxygen production. Another quantity that was varied in the runs described below was the concentration of sodium hydroxide; accordingly its effect on the catalyzed rate was determined with the result:

[NaOH]	[ClO$^-$]	Gas rate
0.170 *M*	0.935 *M*	1.405 ml./min.
0.622	0.910	1.361

The amount of copper was constant. The change in rate is very close to that to be expected from the fall in the sodium hypochlorite concentration. Hence sodium hydroxide does not affect the rate. The temperature dependence of the rate was of course important, and similar measurements were made at 30 and 40°C. These gave an over-all energy of activation of 15.5 kcal./gm-mol. for the gas evolution.

6. Runs with Complexing Anions

The general procedure was to add known amounts of copper chloride to sodium hypochlorite solution, followed later by known amounts of sodium tellurate or periodate, or the sodium salt of any other anion being investigated. The rates of oxygen evolution under the various conditions were then measured; as always it was necessary to allow some time to elapse after any change for the gas rate to reach a steady value. The results are given in Table II.

TABLE II

Run	Temp., °C.	Vol. of solution, ml.	[ClO$^-$] (mean)	[Cu] (total)	[Anion] (total)	Gas rate, ml. NTP/ min.	Remarks
1	40°	581.5	0.98*M*	$4.76 \times 10^{-5}M$	$2.69 \times 10^{-3}M$	0.0157	Tellurate added
2	50°	800	0.90	1.73×10^{-5}	0	0.943	
			0.81	1.73×10^{-5}	2.73×10^{-3}	0.048	Periodate added
3	40°	511.5	1.65	1.082×10^{-4}	0	2.96	
			1.55	"	4.56×10^{-5}	2.10	Periodate added
			1.47	"	13.68	1.00	
			1.41	"	22.8	0.194	
			1.38	"	31.9	0.021	
4	40°	555	0.885	1.074×10^{-4}	0	1.57	
			0.85	"	3.65×10^{-5}	1.195	Periodate added
			0.825	"	7.3	0.945	
			0.80	"	10.95	0.695	
			0.77	"	14.6	0.47	
			0.745	"	18.25	0.25	
			0.725	"	21.9	0.115	
5	40°	573	1.65	0	0	0.0170	Effect of NaOH on equilibrium with periodate

TABLE II (*concluded*)

Run	Temp., °C.	Vol. of solution, ml.	[ClO⁻] (mean)	[Cu] (total)	[Anion] (total)	Gas rate, ml. NTP/ min.	Remarks
5	40°	573	1.55*M*	0	20.4×10^{-5}	0.0160	NaOH Na_2CO_3
			1.52	9.67×10^{-5}	"	0.687	0.382 0.029*M*
			1.48	"	"	0.637	0.695 0.036
			1.45	"	"	0.631	0.942 0.045
6	40°	543.5	1.58	1.008×10^{-4}	0	2.78	
			1.50	"	21.4×10^{-5}	0.216	Periodate added
7	40°	538	1.33	5.15×10^{-5}	0	1.218	
			1.30	"	10.52×10^{-5}	0.196	Periodate added
8	30°	573.5	1.355	8.41×10^{-5}	16.8×10^{-5}	0.087	Periodate
	40		1.34	"	"	0.235	added
	50		1.315	"	"	0.568	
	50		1.29	"	3.96×10^{-3}	0.053	
9	40°	587	1.30	16.34×10^{-5}	0	4.28	0.400 *M* NaOH
			1.25	"	13.15×10^{-5}	1.65	Tellurate added
			1.23	"	26.3	0.187	
			1.20	"	32.9	0.069	
10	50°	587	1.18	16.34×10^{-5}	32.9×10^{-5}	0.208	Tellurate added 0.400 *M* NaOH
11	60°	587	1.15	16.34×10^{-5}	32.9×10^{-5}	0.610	Tellurate added 0.400 *M* NaOH
12	40°	557.5	1.25	1.72×10^{-4}	0	3.81	0.400 *M* NaOH
			1.18	"	0.673×10^{-4}	2.42	Tellurate added
			1.12	"	2.02	0.605	
			1.10	"	4.035	0.0255	
13	40°	576	1.28	1.663×10^{-4}	33.55×10^{-5}	0.037	0.162 *M* NaOH
	50		1.22	"	"	0.1165	0.162 *M* NaOH
	50		1.18	"	"	0.217	0.471 *M* NaOH
14	50°	576	1.13	1.663×10^{-4}	5.80×10^{-3}	0.043	Tellurate added
15	50°	586	1.17	1.634×10^{-4}	33.0×10^{-5}	0.1085	2.27 *M* NaCl
			1.15	"	"	1.102	2.57 *M* NaCl
			1.13	"	"	0.104	2.87 *M* NaCl
16	40°	564	1.25	1.70×10^{-4}	0	3.84	Stannate added
			1.23	"	1.40×10^{-4}	4.59	
			1.21	"	4.89	4.76	
17	40°	594	1.25	1.62×10^{-4}	3.29×10^{-4}	4.75	Stibnate added
		619	1.18	1.55	19.7	4.60	
18	40°	620	1.15	1.55×10^{-4}	3.65×10^{-3}	4.38	Selenate added

DISCUSSION OF RESULTS

The general assumption that we shall make in interpreting these results is that the rate before and after the addition of the complexing agent gives the fraction of the copper that is not complexed and still present as $Cu(OH)_4^-$. The rates are first to be corrected for the uncatalyzed evolution of oxygen,

and allowance has to be made for the fall in hypochlorite concentration. With this assumption we have enough data for the determination of the equilibrium constant for the decomposition of the complex ion into simple ions. There is some justification of this general assumption from the results in Table II. Firstly, as will be seen in more detail later, there is the internal consistency of the results; and, secondly, there is the fact that a large excess of periodate or tellurate reduces the rate to the uncatalyzed rate, since now virtually all the copper is complexed. The uncatalyzed rates calculated for the conditions in runs 1, 2, 8 (last part), and 14 are

Run	Obs. rate	Calc. rate
1	0.0157	0.0145 ml./min.
2	0.048	0.049
14	0.043	0.049
8	0.053	0.056

In runs 1 and 14 excess tellurate was present; in runs 2 and 8 excess periodate.

Another point that must be considered is whether an appreciable fraction of the copper present is divalent. It seems reasonable to suppose that when a trivalent copper atom catalyzes the decomposition of a hypochlorite ion, it is reduced to divalent copper, which is subsequently oxidized back by more hypochlorite. This oxidation can be observed qualitatively by means of the color change when copper chloride is added to sodium hypochlorite: small amounts of copper at room temperature (20°C.) are oxidized very rapidly, the color change appearing complete virtually as soon as the solutions are mixed and certainly within a second or two. At the same temperature 1 ml. of 0.0277 *M* copper chloride added to hypochlorite gave an oxygen evolution of 0.25 ml./min. This corresponds to 2.77×10^{-5} gm-atoms of copper liberating 2.2×10^{-5} gm-atoms of oxygen every minute, or one atom of oxygen per copper atom every 76 sec. Thus at the most perhaps 2% of the copper could be divalent; this is an upper limit since each reduction of trivalent copper might give more than one oxygen atom. We cannot suppose that more than one copper atom is involved per oxygen atom, or the reaction would not be first order in copper.

Since the ionic strengths of the solutions are quite large, the calculated equilibrium constants will not be the true thermodynamic equilibrium constants, since we have ignored, or rather failed to evaluate, the activity coefficients. The uncomplexed copper concentration, although found from a rate of reaction, is really a concentration and not an activity. If c_1 is the total copper concentration before complexing, when the reaction goes at a rate r_1; and if c_2 is the concentration of uncomplexed copper after periodate is added, etc., when the rate of reaction is r_2, then

$$\frac{r_2}{r_1} = \frac{a_2}{a_1} = \frac{c_2 f_2}{c_1 f_1}$$

where a and f are the corresponding activities and activity coefficients. The calculated value of c_2 is taken to be

$$c_2(\text{calc.}) = c_1 \cdot \frac{r_2}{r_1} = c_2 \cdot \frac{f_2}{f_1}.$$

In practice, since the ionic strength remains virtually constant throughout a run, f_2 will be very nearly equal to f_1, so that c_2(calc.) = c_2. Hence the equilibrium constants reported below are ratios of concentration, not activity. It is impractical to use this experimental method at low ionic strength, since we need a considerable concentration of hypochlorite to ensure a rapid oxidation of any divalent copper.

The calculation of equilibrium constants was done by the following equations. As we shall see in a moment the results support the view that only 1-1 complexes of formula Cu(anion), or 1-2 complexes of formula Cu(anion)$_2$, are formed. Let K_1 be the equilibrium constant for the reaction;

$$\text{Cu(111)} + \text{anion} \longrightarrow \text{1-1 complex}$$

so $K_1 = \dfrac{[\text{Cu}].[\text{anion}]}{[\text{1-1 complex}]}$.

Let K_2 similarly be the constant for:

$$\text{Cu(111)} + 2\ \text{anion} \longrightarrow \text{1-2 complex}$$

so $K_2 = \dfrac{[\text{Cu}].[\text{anion}]^2}{[\text{1-2 complex}]}$.

Let a = total concentration of copper;
let ay = total concentration of the complexing anion, and
let p = fraction of the gas rate that remains after the complexing anion is added. Then our assumption means that

$$[\text{Cu}] = ap.$$

There are also equations for the mass balance of the copper:

$$a = [\text{Cu}] + [\text{1-1 complex}] + [\text{1-2 complex}]$$

and of the anion:

$$ay = [\text{anion}] + [\text{1-1 complex}] + 2[\text{1-2 complex}].$$

Eliminating the unknown concentrations of the anion and the complexes, these equations lead to

$$\text{[i]} \qquad K_2(K_1 - ap)\left\{\frac{(1-p)}{p}K_1 - a(y - 1 + p)\right\} = a^2K_1^2(y - 2 + 2p)^2.$$

This equation enables us to evaluate K_1 and K_2 if we find the gas rate for two values of y, which is the ratio of the total anion to total copper present. It leads in two particular cases to simpler equations which are of interest. Firstly, if only the 1-1 complex is formed, K_2 is infinite, and equation [i] reduces to

$$\text{[ii]} \qquad K_1 = \frac{ap}{1-p}(y - 1 + p).$$

Secondly, if only the 1-2 complex is formed, K_1 is infinite, and equation [i] reduces to

$$\text{[iii]} \qquad K_2 = \frac{a^2p}{1-p}(y - 2 + 2p)^2.$$

These simpler equations are of use in obtaining approximate values of the constants.

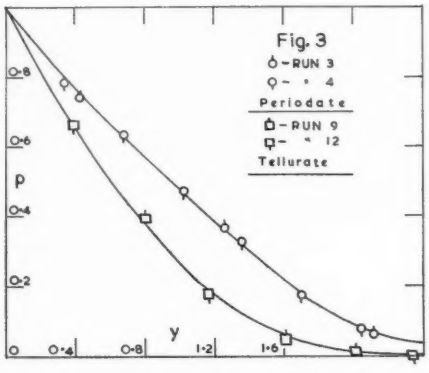
Equations [ii] and [iii] also show that, in a plot of y against p, if only a stable 1-1 complex is formed, so that K_1 is small and K_2 large, then the points will

TABLE III

Run	Temp., °C.	R_0 (calc.)	Rate (corr.)	y	p	
3	40°	2.79	2.08	0.422	0.745	
		2.66	0.98	1.265	0.368	
		2.56	0.176	2.108	0.0688	
		2.53	0.003	2.951	0.0012	
4	40	1.51	1.185	0.340	0.787	
		1.47	0.935	0.680	0.636	
		1.43	0.685	1.021	0.478	
		1.39	0.46	1.361	0.330	
		1.35	0.24	1.702	0.178	
		1.32	0.105	2.042	0.0795	
6	40	2.68	0.194	2.098	0.0724	
7	40	1.18	0.178	2.042	0.151	
8	30	0.91	0.081	1.999	0.089	
	40	2.08	0.216	1.999	0.104	
	50	4.50	0.511	1.999	0.114	
9	40	4.13	1.63	0.805	0.395	
		4.07	0.168	1.610	0.0413	
		3.98	0.051	2.012	0.0128	
10	50	8.65	0.156	2.012	0.0180	
11	60	17.1	0.464	2.012	0.0272	
12	40	3.60	2.40	0.391	0.667	
		3.44	0.59	1.173	0.172	
				2.346	0.003	
13	40	3.96	0.0185	2.018	0.00465	(0.162 *M* NaOH)
	50	8.36	0.0632	2.018	0.00755	(0.162 *M* NaOH)
	50	8.12	0.166	2.018	0.0205	(0.471 *M* NaOH)
15	50	8.06	0.0725	2.018	0.0090	(2.27 *M* NaCl)
		7.94	0.0565	2.018	0.0084	(2.57 *M* NaCl)
		7.82	0.069	2.018	0.0088	(2.87 *M* NaCl)

fall near the line $y + p = 1$. Similarly if only a stable 1-2 complex is formed, so that K_1 is large and K_2 small, then the points fall near the line $y + 2p = 2$. Table III gives the values of y and p calculated from the results of Table II, and some of these are plotted in Fig. 3.

In Table III the column headed R_0(calc.) gives the calculated value of what the rate would be if no periodate or tellurate had been added. In the next column is the observed rate corrected for the uncatalyzed rate, and p is the ratio of these two quantities. From Fig. 3 it is evident that in the copper periodate system the most stable complex is the 1-2 complex, with evidence of a much less stable 1-1 complex. The same is true of the copper tellurate system, except that the 1-1 complex is considerably more stable. To evaluate the constants the values of p at $y = 1$ and $y = 2$ were interpolated on the best line through the experimental points, and these values were substituted



in equation [i]. The constants so found for 40°C. are:

	TELLURATE	PERIODATE
K_1	1.8×10^{-6}	3.4×10^{-5}
K_2	1.1×10^{-11}	8.0×10^{-11}

The fit given by these constants is shown in Fig. 3, where the solid line through the experimental points is obtained by substituting these values of K_1 and K_2 in equation [i] and plotting the resulting curve. The fit seems adequate, though on account of experimental error the accuracy is not high. The points used are from runs 3 and 4 for periodate, and runs 9 and 12 for tellurate; there are small differences in the copper concentrations between these runs so a mean value was used in the calculations. Both K_1 and K_2 are sensitive to errors in p, as can be seen by putting $y = 2$ in equation [iii] which then becomes approximately $K_2 = 4a^2p^3$. It cannot be claimed that the possible error in the constants is less than perhaps 20%. Runs 6, 7, and 8 agree with the constants so evaluated. By substituting K_1 and K_2 at the appropriate values of a and y in equation [i] values of p can be calculated to compare with the experimental ones, with the result:

RUN	p(OBS.)	p(CALC.)	a
6	0.072	0.072	10.1×10^{-5}
7	0.145	0.140	5.15
8	0.104	0.107	8.4

As these values of p agree over a range of copper concentrations, this shows that (as assumed above) there is one copper atom in the complex. The point may also be made here that it is impossible to obtain a curve anywhere near all the experimental points by assuming only a 1-1 or only a 1-2 complex. A 1-2 complex alone cannot give points below the line $y + 2p = 2$. A 1-1 complex alone gives a curve which, if it fits the experimental points at $y = 1$, is much too high at $y = 2$: for periodate the value of p at $y = 2$ would be 0.265 (obs. 0.09); for tellurate the value would be 0.085 (obs. 0.013).

Run 5 shows that varying the concentration of sodium hydroxide has little effect on the oxygen rate in copper periodate, at least when roughly two periodates are present per copper atom. The equation for the formation of the complex is therefore presumably one which does not involve OH^- ions. Rae (8) found periodic acid to be effectively dibasic with dissociation con-

stants about 2.3×10^{-2} and 10^{-6}. Hill's results (5) show that the solid phase in contact with a saturated solution containing 0.11 *M* or more sodium hydroxide is $Na_3H_2IO_6$. Thus presumably the third dissociation constant is greater than 10^{-13}. As the concentration of sodium hydroxide in the present work was 0.38 *M* or greater, the free periodate ions would be mostly $H_2IO_6^{-3}$, and this would make the reversible reaction whose constant is K_2

$$Cu(OH)_4^- + 2\ H_2IO_6^{-3} \rightleftharpoons Cu(IO_6)_2^{-7} + 4\ H_2O. \qquad [a]$$

This is admittedly a very large charge on an ion, but it is a large ion, and its formula is supported by the solid $Na_7Cu(IO_6)_2.16H_2O$ which separates from more concentrated solutions.

Run 8, in combination to a lesser extent with other runs, gives information about the variation with temperature of the equilibrium constant for the copper periodate system from results in the neighborhood of $y = 2$, when the 1-2 complex is the chief one formed. These results were therefore treated as follows. K_2 was calculated by the approximate formula, equation [iii], and from its variation a heat of reaction for the reaction [*a*] given above was deduced. The results of run 8 give:

Temperature:	30°	40°	50°C.
K_2(approx.):	2.2	3.4	4.7×10^{-11}.

This makes the reaction giving the complex ion exothermic by $7\frac{1}{2}$ kcal. (perhaps $\pm$ 1 kcal.). These approximate values of K_2 differ by a factor of about 2 from the more accurate ones owing to the presence of the 1-1 complex; but they probably give a fair estimate of the temperature variation of K_2, and hence of the heat of reaction.

Similarly for the copper tellurate complex the effect of sodium hydroxide is found from runs 9, 10, and 13. This effect can be seen in Table IV, where values of the approximate K_2 (from equation [iii]) are given.

TABLE IV

Run	Temp., °C.	[NaOH]	K_2 (approx.)	K_2/[NaOH]	K_2/[NaOH]^2
13	40°	0.162 *M*	0.91×10^{-13}	5.6×10^{-13}	35×10^{-13}
9	40°	0.400	4.9	12.2	31
13	50°	0.162	2.3	14	87
10	50°	0.400	11.3	28	71
13	50°	0.471	20.1	43	91

It is evident that K_2 is roughly proportional to [NaOH]^2. Run 15 was made to check that sodium chloride did not cause a comparable effect, either through some unknown reaction of the chloride ion or through changes in ionic strength; as can be seen from Table II sodium chloride had a negligible effect.The exact reaction with tellurate is less certain than with periodate. Blanc (1) found telluric acid to be dibasic, with dissociation constants 7×10^{-7} and 4×10^{-11}. However salts up to $M_4H_2TeO_6$ are known (the compound Ag_6TeO_6

may well be covalent). If we have $H_2TeO_6^{-4}$ ions in alkaline solution (pH above 13) the reversible reaction would be:

$$Cu(OH)_4^- + 2\ H_2TeO_6^{-4} \rightleftharpoons Cu(HTeO_6)_2^{-7} + 2\ OH^- + 2\ H_2O.$$

$H_4TeO_6^{-2}$ ions would require the complex to be $Cu(H_3TeO_6)_2^{-3}$. Runs 9, 10, and 11 give results at different temperatures, and treating them as for the copper periodate complex, the results give:

Temperature:	40°	50°	60°C.
K_2(approx.):	4.9	11.3	33×10^{-13}.

This makes the heat of reaction close to 20 kcal.

Finally in runs 16, 17, and 18 the chemically somewhat similar ions, stannate, stibnate, and selenate, were examined. No sign of a reduction in the rate of oxygen evolution was observed; presumably therefore no analogous complex ions are formed. In fact with stannate there was some enhancement of the rate, the reason for this being at present unknown. It should be added, to complete the picture with periodate and tellurate, that it was found that these ions, when no copper was present, had no effect on the rate.

REFERENCES

1. Blanc, E. J. chim. phys. 18: 28. 1920.
2. Brauner, B. and Kuzma, B. Ber. 40: 3362. 1907.
3. Chirnoaga, E. J. Chem. Soc. 1693. 1926.
4. Crum, W. Liebigs Ann. Chem. 55: 213. 1845.
5. Hill, A. E. J. Am. Chem. Soc. 50: 2678. 1928.
6. Krüger, M. Pogg. Ann. 62: 447. 1844.
7. Malatesta, L. Gazz. chim. ital. 71: 467 and 580. 1941.
8. Rae, N. J. Chem. Soc. 876. 1931.
9. Scholder, R. and Voelskow, U. Z. anorg. Chem. 266: 256. 1951.

COMPARISON OF BARLEY GUMS ISOLATED BY VARIOUS PROCEDURES[1]

By W. O. S. Meredith, T. A. Watts, and J. A. Anderson

ABSTRACT

A barley gum that is believed to be the undegraded, water-soluble, nonstarch polysaccharide of the grain has been isolated. Aqueous solutions of this gum are extremely viscous and are stable. Enzymes that degrade gum during simple aqueous extraction were inactivated first by refluxing barley grist in boiling 85% alcohol followed by extraction of the dried grist with a 1% solution of papain. Gums of lower degree of polymerization, as judged by viscosity measurements, were obtained by aqueous extraction and acid treatments. Two enzyme systems that degrade gums are thought to be present in barley. One (which is inactivated by alcohol) degrades the initially soluble gum and brings an initially insoluble form into solution. The second system (which is inactivated by papain) accompanies and degrades the initially soluble gum during aqueous extraction or in aqueous solutions of the preparation. The purest gum contains only 0.1% nitrogen, and this may be part of the molecular complex. Mild, cold, alkali treatment of this gum reduces molecular size considerably as measured by viscosity of solutions. "X"-enzyme isolated from a bacterial source cleaves the gum into two oligosaccharides of glucose and a component containing D-glucose, L-arabinose, D-xylose, and D-galactose. No free sugars are produced.

Changes in endosperm structure during malting of barley are assumed to be brought about by dissolution of the hemicellulose material of cell walls by cytases, and cell constituents are thus exposed to attack by amylolytic and proteolytic enzymes. Little is known about either the cereal hemicelluloses or the cytases, but the cell wall materials are now considered to be complex polysaccharides that resemble the plant gums in composition and properties (12, 14). Isolation of these in native form clears the way for the study of their properties and composition and for studies of the enzymes that degrade them. An additional key to understanding the malting process may thus be obtained.

Barley and malt gums—water-soluble, nonstarch polysaccharides containing D-glucose, L-arabinose, and D-xylose—and enzymes that degrade them are being studied intensively in several laboratories (2, 3, 4, 10, 14, 16, 17), and there is general agreement that these gums and their degradation products contribute markedly to wort and beer viscosity and perhaps to other beer properties (9, 13). Degradation of the gums by enzymes, presumably cytases or hemicellulases, is accompanied by decrease in solution viscosity (14, 16, 17); indeed change in viscosity of solution is the best measure of enzymatic activity (2, 17). There are some differences in composition and properties of gums recovered in the same way from barley and malt (10, 15, 16), and these differences may well reflect the changes that take place in the kernel when barley "modifies" to become malt. The barley gum is changed during malting, but it is not clear yet whether it disappears and is replaced by other nonstarch polysaccharides that were insoluble in the barley or whether much of the barley

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gum is still recoverable as malt gum (10, 14, 15, 16). This problem can only be resolved by preparation of pure isolates from raw barley, growing barley, and from malt, that can be directly compared for composition and properties. Such isolates would also be ideal substrates for detection and measurement of enzymatic activity. Preparation of such isolates is fraught with many difficulties, chiefly arising from enzymatic degradation of material during extraction. Gums produced in earlier studies in this laboratory (10) were unstable in solution, presumably because of contamination with enzymes. A method has now been devised, and is here described, for isolation of barley gum that appears to be degraded to a minimum extent. This isolation method will later be applied to germinating barley and to malt.

Preece, Ashworth, and Hunter (15) refluxed barley grist in boiling alcohol in order to inactivate enzymes present in barley, and recovered and dried the grist before extracting the water-soluble gums. A similar procedure was included in the studies reported in this paper, but additional treatment with a proteolytic enzyme was required before a barley gum that was stable in aqueous solution was obtained. The final product produced extremely viscous, stable, aqueous solutions. It contains the same sugars found previously—D-glucose, L-arabinose, and D-xylose, and a trace of D-galactose—and may well be the naturally occurring material. Nitrogen content of gum was finally reduced to less than 0.1%. Various acid, precipitation, and enzymatic treatments were used to reduce the nitrogen content of gum; the results thus provide information on the role of nitrogen in the gum and its influence on some properties.

MATERIALS AND METHODS

Barley

Further aliquots of the barley that was used in previous studies (10), namely Montcalm barley grown at the University of Manitoba in 1949, were used. Barley grist was prepared by grinding 500-gm. lots in a Wiley mill with a 1 mm. sieve.

Alcohol Treatment of Barley Grist

Grist was boiled under reflux for 30 min. with five parts of 85% ethyl alcohol (specific gravity 0.85). The cooled mixture was centrifuged and the extracted grist was air-dried. Specific gravity of the alcohol must be adjusted carefully as variations in strength of alcohol produce variations in gum properties. This treatment is similar to that used by Preece *et al.* (15), except that a single rather than a double alcohol treatment is used.

Preparation of Gum

The basic procedure was extraction of barley grist, raw or alcohol treated, with eight parts of water at room temperature for two hours with continuous stirring (10). The spent grains were removed by centrifuging and the gum was precipitated by adding the liquor to three volumes of ethyl alcohol. The product was recovered by centrifuging and solvent exchange using ethyl alcohol, acetone, and ether (10).

Additional treatments of mash or liquor were also studied. These were the addition of trichloroacetic acid, hydrochloric acid, or papain, to the liquor or to the mash. Addition of such agents to the liquor is termed "precipitation method" in this report, and addition to the mash is called "extraction method". Details of the various procedures are given below.

Precipitation Method

The three precipitants were allowed to remain with the liquor for 15 min. before proceeding to the next stage of the procedure. Trichloroacetic acid was added to the liquor to produce a 6% concentration; any precipitate was removed before the liquor was added to alcohol. Sufficient hydrochloric acid was added to the liquor to bring the pH to that produced by 6% trichloroacetic acid; this value was pH 1.0. Powdered papain was ground into solution with distilled water and undissolved material was removed by centrifuging. Sufficient solution was added to the liquor to bring the concentration of papain to 1%. The papain was precipitated by making the solution to 6% concentration of trichloroacetic acid, and the precipitate was removed by centrifuging.

Extraction Method

Barley grist was extracted by 6% trichloroacetic acid, hydrochloric acid of pH 1.0, or 1% papain solution for two hours at room temperature as in the regular procedure. Papain was removed by the trichloroacetic acid treatment described above for the precipitation method.

Gum Characteristics

Viscosity and Concentration

One per cent solutions were prepared by mixing gum and distilled water and stirring the mixture till the gum was dispersed. Dispersion was assisted by heating the solution to about 90°C. for 10 min. Insoluble material was removed by centrifuging. Viscosity measurements were made in an Ostwald viscosimeter at 30°C. within about an hour after preparation of solution and again after 24 hr. Concentration of gum was determined by drying an aliquot of solution at 105°C. overnight.

Nitrogen Determination

A modified micromethod similar to that used by Levi and Anderson (7), but using sodium sulphate and mercuric sulphate instead of selenium, was employed. The experimental error was less than 4% of the amount of nitrogen determined.

Sugar Components

Small samples of gum (about 30 mgm.) were hydrolyzed with 1 ml. of normal sulphuric acid in sealed tubes for 16 hr. The hydrolyzate was neutralized by passage through Duolite A-7 resin and the percolate dried by distillation under reduced pressure.

Chromatographic examination of the mixed sugars in the residues was made using the same solvents and procedures described previously (10). The aniline

phosphate spray of Bryson and Mitchell (5) was used for locating the sugar spots.

Amino Acid Components

Gums were hydrolyzed in the same way as for sugar identification, but with normal hydrochloric acid. Salts were removed by repeated distillation under reduced pressure.

Resolution of the amino acids in the residues was obtained by means of the solvents butanol/acetic acid/water in ratios 4:1:5 (8, 11) and butanol/benzene/pyridine/water in ratios 4:2:2:5 (8). The paper was Whatman No. 1 and the colors were developed by spraying with 0.1% ninhydrin in butanol and drying at 90°C. for 10 min. Proline was identified by isatin in acid butanol (1).

RESULTS AND DISCUSSION

The investigation developed into a factorial study of raw and alcohol-treated barley treated with each of two acids, trichloroacetic acid and hydrochloric acid, and one enzyme, papain. These acids and papain treatments were applied to the aqueous extracts of the barley and also as extracting solutions. The resulting data may be presented in many ways, but for convenience they are given in Table I in a standard form for a factorial experiment. This permits

TABLE I

DATA FOR BARLEY GUMS OBTAINED BY DIFFERENT PROCEDURES

Property	Precipitation method							
	Raw barley extract				Alcohol-treated barley extract			
	(1) Water	(2) T.C.A.*	(3) HCl	(4) Papain	(5) Water	(6) T.C.A.*	(7) HCl	(8) Papain
Yield, %	3.4	2.1	2.7	1.8	1.1	1.1	1.1	0.9
Nitrogen, %	3.00	0.50	2.14	0.12	0.46	0.50	0.30	0.07
Viscosity of aqueous solution, cp.	2.34	3.55	2.77	4.07	48.2	64.1	33.3	75.8
Viscosity reduction after 24 hr., %	50	1.7	1.1	1.0	62	61	3.0	1.0
	Extraction method							
	Raw barley				Alcohol-treated barley			
	(1) Water	(2) T.C.A.*	(3) HCl	(4) Papain	(5) Water	(6) T.C.A.*	(7) HCl	(8) Papain
Yield, %	3.4	2.3	2.8	1.7	1.1	1.5	1.8	1.3
Nitrogen, %	3.00	0.73	1.97	0.12	0.46	0.50	0.82	0.08
Viscosity of aqueous solution, cp.	2.34	12.8	11.8	3.66	48.2	32.1	44.8	752.0
Viscosity reduction after 24 hr., %	50	21	10	1.0	62	18	13	2.9

**Trichloroacetic acid.*

ready comparison of all sets of data. Each of the four sections contains the comparable data for water, trichloroacetic acid, hydrochloric acid, and papain procedures. These are related in that hydrochloric acid was used as a means of separating the effect of acidity of trichloroacetic acid from its precipitating effect, and trichloroacetic acid was used to remove papain from its solution before gum was precipitated.

The comparison between simple aqueous extraction of raw and alcohol-treated barley is discussed in the following subsection, and this is followed by discussion of acid treatment of the aqueous extracts. The methods of extraction are compared with each other and with the "precipitation" procedures in the third subsection. The use of papain as a precipitant and as an extracting agent is discussed in the fourth subsection and compared with the other treatments in the fifth subsection. The next subsection deals with certain properties of the gum obtained by papain extraction of alcohol-treated barley, or "papain" gum. This is followed by a general discussion of the results in relation to other studies.

Effect of Alcohol Treatment of Barley

The simple effect of refluxing the barley grist in boiling 85% alcohol prior to extraction of gum is demonstrated by comparison of columns 1 and 5 in the upper half of Table I. The gum from alcohol-treated barley is lower in yield and nitrogen content than that from raw barley. These changes are accompanied by a marked increase in solution viscosity, but stability of gum solution (measured by viscosity reduction after 24 hr.) is not improved.

The characteristics of the gum from raw barley are practically identical with those reported previously (10), and the same sugars, D-glucose, L-arabinose, and D-xylose, were found in the gum. Although the properties of the gum from alcohol-treated barley were different from those of the gum from raw barley, there was no change in sugar composition as judged by appearance of chromatograms of acid-hydrolyzed gums.

The differences between the two gums in yield and solution viscosity are in accord with the suggestion of Preece and Ashworth (14) that barley contains two types of nonstarch polysaccharides of similar composition that are attacked by an enzyme system present in barley. One type is the true water-soluble gum, and this is reduced in molecular complexity by the enzyme system during extraction. The other type is initially less soluble, but its solubility is increased by action of the enzyme system. Our results suggest that this enzyme system was inactivated by the boiling alcohol extraction, so that the product from treated barley is likely to be the true initially soluble polysaccharide.

The instability of solutions of the gum from alcohol-treated barley was somewhat surprising in view of the marked increase in solution viscosity. The latter condition is an indication that the gum was in a more highly polymerized state than that from the raw barley. Refluxing the gum in boiling alcohol failed to improve stability, but boiling of aqueous solutions of gum improved stability of the recovered product (2). Other methods were therefore attempted.

A suggestion had been made previously that nitrogen complexes may play some role in determining the viscosity and stability of gum solution (9, 10). The data in Table I support this view, as the gum from alcohol-treated barley is considerably lower than the raw-barley gum in nitrogen content, and certain amino acids—leucine, isoleucine, valine, and proline—present in the latter, were not detected in the former. Alcohol treatment of barley grist therefore has lowered nitrogen content of gum, and removed certain types of nitrogen complexes, but an "instability factor", probably an enzyme system, survives this treatment.

Effect of Acid Treatments of Barley Extracts

Columns 2 and 3 of the upper half of Table I contain data on the effect of acid treatment of the aqueous extracts of raw barley on the gum properties. Columns 6 and 7 give information on comparable gums obtained from alcohol-treated barley.

Trichloroacetic acid treatment reduced yield and nitrogen content of gum from raw barley and increased solution viscosity and stability. Hydrochloric acid had much the same effect but yield and nitrogen content reductions were not as great.

Yield and nitrogen content of gums produced from alcohol-treated barley by the acid treatments were not affected. The trichloroacetic acid treatment increased solution viscosity but there was no improvement in stability. The hydrochloric acid treatment decreased solution viscosity but improved stability. The net result is that the acid treatments of extraction liquor from alcohol-treated barley produced no improvement in gum properties.

All gums contained D-glucose, L-arabinose, and D-xylose, with D-glucose predominating as judged by area and density of the spots on chromatograms. The amino acid compositions of all gums from raw barley were similar. The composition of gums obtained by acid treatments of alcohol-treated barley differed from that obtained without acid treatment and resembled those from water extracts of raw barley in that leucine, isoleucine, and valine were detected.

The effect of acid treatment of extracts provides further evidence of the mixed character of gum extracted from raw barley. Yields of gum from acid-treated extracts of raw barley are invariably higher than those obtained from similar treatment of alcohol-treated barley, which suggests solution of other material during extraction. But both types of gum are degraded as shown by low solution viscosity. The instability of raw barley gums may be attributed to further degradation of the material that becomes soluble during extraction. This degradation appears to be inhibited by both trichloroacetic acid and hydrochloric acid. Trichloroacetic acid does not appear to inhibit the degradation of the initially soluble gum by factors carried with it.

Effect of Acid Extraction of Barleys

The lower half of Table I contains data for the properties of gums obtained by extraction of barley with acid solutions. The two acids had similar results when applied to raw barley. The increases in viscosity of gum solutions were

relatively great, and although the solutions were more stable than those of the water-extracted gum they were not completely stable. Extraction of alcohol-treated barley with acid solutions increased yield, but solution viscosities were reduced and this may be attributed to impurities in the gum. Stability of solutions was improved, but the net result was no improvement in gum quality. Amino acid and carbohydrate compositions of all gums were similar to those obtained by treatment of the aqueous extracts of raw barley with acid.

Acid extraction of raw barley as compared with acidification of extracts produced gum solutions of higher viscosities. Some control of gum degradation is therefore achieved by acidification of the mash, but the effect is not as great as that obtained by alcohol treatment of the barley. The actions of trichloroacetic acid and alcohol treatments appear to be somewhat similar, but they are not identical and there is an indication that the effects are additive. This suggests that at least two enzyme systems are involved in the degradation of gum during preparation, and that the different treatments inhibit different enzymes.

No acid treatment produced satisfactory gum, but the results indicated that trichloroacetic acid could be safely used as a protein precipitant without seriously altering gum properties. This was important as the next part of the investigation required that papain be removed from solution by some precipitant.

The Effect of Papain as a Precipitant and an Extractant

The failure of acid treatment to improve the quality of gum obtained from alcohol-treated barley suggested that nitrogenous material; possibly associated with contaminants of gum or with instability factors, may be held in fairly close combination with the polysaccharide. Such combinations might be physical or chemical, but they appear to protect the nitrogenous material from denaturation by acid. The possibility of protein elimination by proteolytic enzymes was therefore investigated.

Columns 4 and 8 of the upper section of Table I contain data on gums prepared after addition of papain to water extracts of barley and of alcohol-treated barley. Corresponding data for gums after extraction of both original materials with papain solution are given in the lower section of the table.

The outstanding properties of the gums obtained after papain treatment are low nitrogen contents, and high viscosity and stability of solutions. The instability factor has been eliminated from all four types of gum, but treatments prior to addition of the papain are still reflected in the differences in viscosity of solutions. Although treatment with papain of extracts from raw barley eliminated protein material, the product, as would be expected, produced solutions of low viscosity. Papain treatment of extracts from alcohol-treated barley reduced yield slightly, and the resultant gum was highest of the series in viscosity of solution. This increase in viscosity may be attributed primarily to the stabilization of the solution.

Extraction of barley with papain solution was even more efficient in pro-

duction from alcohol-treated barley of a stable gum with high viscosity of solution; this procedure also stabilized the gum from raw barley. The differences between the gums from raw and alcohol-treated barley were even more striking than previously. Papain treatment produced similar gums from raw barley when used as a precipitant or as an extractant. The results for alcohol-treated barley show the additive effect of alcohol and papain treatments, as the extraction procedure produced gum with highest viscosity of solution (752 cp.) and presumably with the highest degree of polymerization. This "papain" gum appears to be the undegraded, initially water-soluble, nonstarch polysaccharide of barley. Other gums are presumed to be degraded forms of this polysaccharide and some preparations may contain degraded forms of the initially insoluble polysaccharide.

All gums prepared by papain treatment were similar in composition. The principal sugar was D-glucose, but L-arabinose and D-xylose were present, and for the first time in this study D-galactose was identified as a constituent of the gums. Nitrogen content of all gums was low, and only aspartic acid, lysine, serine, glycine, and alanine were identified as amino acid components.

Comparison of Papain with Other Treatments

Although the most striking differences between papain treatment and acid treatments are the stability of all gums obtained by the former treatment and the high viscosity of solution of gum from alcohol-treated barley, there are other interesting differences. Papain reduced nitrogen content of gum to very low levels, and the number of amino acids detected was reduced. Only lysine and serine, and possibly alanine, aspartic acid, and glycine, were common to all gums. Leucine, isoleucine, and valine were present in all gums from raw barley, and in gum obtained by acid treatment of alcohol-treated barley. The removal of protein, and of specific amino acids, by papain indicates that much of the nitrogenous material in the other gums was carried with them as a contaminant. Part may be carried merely because of similar solubility, and part may be bound to the gum in some manner; some of this bound material might be enzymes.

The occurrence of D-galactose in all the gums obtained by papain treatment is also of interest, as this sugar was not detected in hydrolyzates of the other gums in this study. This sugar had been detected in gums prepared previously (10), and its presence might be related to degree of polymerization of gum.

Properties of Gum Obtained by Papain Extraction of Alcohol-treated Barley

As the gum obtained by papain extraction of barley grist that had been refluxed in boiling 85% alcohol is highly viscous in solution and stable, it is believed to most nearly represent the undegraded, initially soluble, nonstarch polysaccharide present in the barley. This seems to be the most desirable material for study of composition and structure, and for use as a substrate for study of enzymes; additional tests were therefore made on this gum to determine its suitability for our purposes. These tests are discussed briefly in the following paragraphs.

Susceptibility to Enzyme Attack

The susceptibility of the "papain" gum to enzymatic degradation was

tested in two ways, the first of which was a check on the presence of active enzymes in the gums obtained when alcohol or papain were not used in the isolation processes.

Aliquots of solutions of other gums were added to portions of a solution of "papain" gum. Addition of 1 ml. of a 1% solution of raw barley gum to 7 ml. of the substrate caused a reduction in viscosity from 69 cp. to 59 cp. in 30 min. Similar results were obtained by addition of a solution of gum obtained directly from alcohol-treated barley; viscosity dropped from 140 cp. to 123 cp. in two hours and to 4 cp. in 24 hr. The presence of enzymes in the crude gums is thus confirmed. The "X"-enzyme described by Bass, Meredith, and Anderson (2) was also tested on the "papain" gum. The concentration of the "X"-enzyme was not known, but a 0.01 ml. aliquot added to 7 ml. of "papain" gum solution reduced viscosity from 375 cp. to 4.5 cp. in three hours. The "papain" gum is therefore a suitable substrate for studies of "X"-enzyme.

Components of Gum

The main component of the gum is D-glucose, but there are appreciable amounts of L-arabinose and D-xylose, and traces of D-galactose; no quantitative measurements of these have been made as yet. In order to study the products of enzymatic hydrolysis, the "papain" gum solution (mentioned above) that was reduced to a viscosity of 4 cp. by "X"-enzyme was dried under reduced pressure and chromatographed. No free sugars were detected, but three spots of low R_g were observed. Larger amounts were then chromatographed, and the three slow moving products were stripped from the paper and hydrolyzed by acid. The slowest moving material produced mainly L-arabinose and D-xylose with some D-glucose and D-galactose. The other two materials produced only D-glucose. These three fractions could not be obtained unless the gum had been degraded by the enzyme system. This suggests the possibility that the gum is composed of several polysaccharides that are either attacked at different rates by the enzyme system, or are released from combination.

The amino acid composition of all gums prepared by use of papain is strikingly similar to that of gum obtained from alcohol-treated barley by simple aqueous extraction. The small amount of nitrogenous material that remains in or with the gums is reasonably constant. This suggests that some protein material that is very difficult to remove from the gums may be part of the molecular complex, or an enzyme-substrate complex, the enzyme moiety of which is inactivated by papain.

Effect of Alkali

Attempts to eliminate nitrogen from the "papain" gum by redispersion in water and addition of trichloroacetic acid failed to remove any nitrogen. The product that was recovered by addition of alcohol was identical with the original in properties. As alkali had been used in previous studies to eliminate nitrogen, it seemed worth while to use alkali treatment on the gum produced by papain treatment.

A number of gums from alcohol-treated barley were tested and all dissolved

readily in normal sodium hydroxide to give 1.0% solutions. Viscosity determinations were made on these solutions, and the results were considerably lower than corresponding values for aqueous solutions. When these gums were recovered from alkaline solution by alcoholic precipitation, etc., and dissolved in water, the viscosities of solutions were around 4 cp. This indicates that they are extremely labile in alkaline solution and suggests that considerable structural changes are brought about in the gum by alkali. Nitrogen content of these gums was not altered by alkali treatment, and no fractions were obtained when solutions were chromatographed in the same way as for enzymatically degraded gum.

As alkali solutions are standard solvents in preparing polysaccharides for studies on structure by means of methylation, and for freeing polysaccharides from protein without change in polysaccharide structure, the results of mild alkali treatment on these barley gums are somewhat curious. Alkali does seem to cause considerable change in molecular complexity of the gums as judged by viscosity of solutions.

Sensitivity of a carbohydrate towards alkali is not common, but our results are not unique, as Wolfrom, Sutherland, and Schlamowitz (18) have recently described a galactogen from beef lung that is degraded by boiling in 30% potassium hydroxide. The sensitivity of barley gum to cold normal alkali does indicate need for cautious interpretation of structural analysis.

GENERAL DISCUSSION

The main object of the investigation was to obtain a barley gum that is highly viscous and stable in solution, and would thus represent as closely as possible the naturally occurring polysaccharide, which is presumably cell wall material. This material and also material closely related to it, but differing in initial water solubility, is degraded during malting and mashing, and the degradation products are important factors influencing the viscosity and perhaps other properties of wort and beer.

A barley gum corresponding closely, it is believed, to the naturally occurring polysaccharide was isolated. It was obtained by inactivating enzymes in the barley by treatment of barley grist with boiling alcohol, extraction of the grain with aqueous papain solution, removal of papain with trichloroacetic acid, and precipitation of gum by alcohol. This product provides a useful reference compound for detailed study of the changes in cell wall material that are brought about by malting and mashing. The gum also appears to merit studies of its structure and to be useful as a substrate for studies of the cytase-like enzyme systems of barley and malt.

Experiences with the various instability factors encountered during the investigation provides information of value in studying the changes in gum characteristics during malting and in elucidating gum structure.

Gum extracted directly with water from raw barley appears to contain material derived from two types of gum—initially soluble gum and another that is initially insoluble but is made soluble during extraction. This is in accord with the concept of Preece and Ashworth (14).

Evidently there are two main enzyme systems that degrade the nonstarch polysaccharides. One of the systems is inactivated by alcohol treatment and the other by papain. Both enzyme systems must be inactivated in order to obtain initially soluble gum in uncontaminated and undegraded form. Papain extraction produced more gum from raw barley than from alcohol-treated barley, so that the former product may be assumed to contain a mixture similar to that in preparations obtained by aqueous extraction of raw barley. All the material is degraded to some extent, but the product is stable in solution. One may then postulate that the enzyme system inactivated by alcohol can reduce both types of gum—soluble and initially insoluble—to a fairly low degree of polymerization even in the presence of papain. When this system is inactivated by alcohol treatment the bringing into solution of the initially insoluble material is prevented and the initially soluble material is degraded at a slow rate, or in a different way, by the other enzyme system that is finally inhibited by papain. This papain-sensitive system may be more specific in its action than the other system. These two enzyme systems are probably extremely important in the malting process and will be studied in later investigations.

All gums contain mainly D-glucose, but L-arabinose and D-xylose are also present. But there are two distinctions between the "papain" gum and the other gums worth mentioning. The first is the presence of D-galactose in the "papain" gum, and this might be related to molecular complexity. The second is the considerably reduced nitrogen content. A high precentage of the nitrogen in the crude gums is extraneous material precipitated with the polysaccharides, but the purest gum still contains around 0.1% nitrogen. This could be within the error of measurement, but hydrolysis of the "papain" gum produced free amino acids that were detected by chromatography. This small amount of nitrogenous material may then be an integral part of the whole gum—a cement that holds the polysaccharide together. Convincing evidence of a protein-carbohydrate linkage is lacking, and will be difficult to provide. The reaction of gum with relatively mild alkali provides some information on this point.

The "papain" gum is sensitive to a normal solution of sodium hydroxide. Viscosity of the alkaline solution is much lower than that of water solutions. Solution viscosity of recovered material is around 4 cp. as compared with the original value of around 750 cp. If polysaccharide structure is not affected by alkali, then the alkali must have acted on the small amount of residual nitrogenous material in the gum, and thereby reduced molecular size. This mechanism seems possible if the protein is acting as a binding agent that holds some polysaccharide mixture together. However, no fractions were obtained when the alkali treated gum was chromatographed in the same way as gum that had been hydrolyzed by enzymes. The alternative is to assume that cold alkali treatment which is relatively mild in terms of alkaline treatments commonly used in carbohydrate chemistry depolymerizes the polysaccharides to an appreciable extent. The resolution of these alternatives must await detailed study of gum components and structure.

Since the above phases of our work have been completed, Preece and Mackenzie (16) have published a description of fractionation of barley gum. They

obtained a pure laevorotatory polyglucosan by treatment of extract liquor of barley with graded amounts of ammonium sulphate. A preliminary study of their procedure indicates that a pure laevorotatory polyglucosan can also be obtained from a papain extract of our alcohol-treated barley grist, and less readily from a solution of "papain" gum. This polyglucosan is quite viscous in solution, and is thus a useful addition to available substrates for testing cytolytic activity. Its properties and relation to the original gum will be studied. However, it seems advisable to recall that ammonium sulphate is recognized as a peptizing agent for proteins.

Structural studies have been commenced at the University of Minnesota, and Gilles, Meredith, and Smith (6) have reported on a preliminary investigation made with the gum isolated by aqueous extraction from alcohol-treated barley. Methylation of the gum either directly or through its acetate provided a methylated product that was fractionated into three components. These were: (*a*) a methylated araboxylan ($[\alpha]_D - 160°$ in acetone), (*b*) a methylated poly-α-glucosan ($[\alpha]_D + 158°$ in acetone), and (*c*) methylated poly-β-glucosan ($[\alpha]_D - 9°$ in acetone). Results of chemical fractionation of the gum obtained by papain treatment of alcohol-treated barley are not yet available, but the enzymatic hydrolysis of this gum by "X"-enzyme produced three fractions—a pentosan and two oligoglucosides—which are strikingly similar to those obtained by Gilles *et al.*

Concurrent studies of chemical and enzymatic hydrolysis of gum, or gum fractions, are thus proving useful and complementary in elucidating the molecular architecture of the nonstarch polysaccharides of barley.

REFERENCES

1. Acher, R., Fromogeot, C., and Jutisz, M. Biochim. et Biophys. Acta, 5: 81–88. 1950.
2. Bass, E. J., Meredith, W. O. S., and Anderson, J. A. Cereal Chem. 29: 262–272. 1952.
3. Bass, E. J., Meredith, W. O. S., and Anderson, J. A. Cereal Chem. In press.
4. Blackwood, A. C. Can. J. Botany, 31: 28–32. 1953.
5. Bryson, J. L. and Mitchell, T. J. Nature, 167: 864. 1951.
6. Gilles, K., Meredith, W. O. S., and Smith, F. Cereal Chem. 29: 314–316. 1952.
7. Levi, I. and Anderson, J. A. Can. J. Research, F, 28: 71–81. 1950.
8. McLeod, A. M. J. Inst. Brewing, 57: 163–169. 1951.
9. Meredith, W. O. S. Ph.D. Thesis. University of Manitoba. 1949.
10. Meredith, W. O. S., Bass, E. J., and Anderson, J. A. Cereal Chem. 28: 177–188. 1951.
11. Partridge, S. M. Biochem. J. 42: 238–248. 1948.
12. Preece, I. A. Wallerstein Labs. Communs. 33: 119–133. 1948.
13. Preece, I. A. European Brewery Convention. Proc. Congr. Brighton 1951. 213–227. 1951.
14. Preece, I. A. and Ashworth, A. S. J. Inst. Brewing, 56: 40–47. 1950.
15. Preece, I. A., Ashworth, A. S. and Hunter, A. D. J. Inst. Brewing, 56: 33–40. 1950.
16. Preece, I. A. and Mackenzie, K. G. J. Inst. Brewing, 58: 353–362. 1952.
17. Sandegren, E. and Enebo, L. J. Inst. Brewing, 58: 198–203. 1952.
18. Wolfrom, M. L., Sutherland, G., and Schlamowitz, M. J. Am. Chem. Soc. 74: 4883–4886. 1952.

THE ELECTRODE BEHAVIOR OF PLATINUM[1]

By A. K. Wiebe and C. A. Winkler

ABSTRACT

A potential of -0.305 ± 0.005 volt (relative to a saturated calomel electrode) was obtained at a freshly prepared platinum surface within 30 sec. of immersion in oxygen-free $N/5$ sulphuric acid saturated with hydrogen. In electrolytes saturated with nitrogen or oxygen potentials of $+0.05 \pm 0.01$ volt and $+0.745 \pm 0.005$ volt respectively were more slowly attained. The times required for the electrode to reach maximum potentials, t_{max}, when it was made a cathode, and corresponding values of t_{max} when it was rendered anodic, were determined over a range of currents. The values of t_{max} appear to provide a method of determining the surface areas of platinum electrodes.

INTRODUCTION

Recent studies in this laboratory (11) with mercury cathodes immersed in $N/5$ sulphuric acid indicated that during electrolysis hydrogen was adsorbed on the mercury cathode such that each surface atom of mercury accommodated one atom of hydrogen. Furthermore, this hydrogen appeared to be retained by the mercury for some time after electrolysis was stopped. Evidence was also obtained which tended to throw some doubt on the validity of the Bowden–Rideal method (2) of area measurement.

Similar experiments with platinum electrodes yielded the results recorded in the present paper.

EXPERIMENTAL AND RESULTS

The cathode ray oscillograph unit and Leeds and Northrup type K potentiometer arrangement were identical with those described in previous papers (7, 8, 10, 11) except that a reversing switch was installed to facilitate reversing the current between the limits of hydrogen and oxygen evolution. The electrolytic cell and experimental methods were also the same in all essential respects. An auxiliary platinum electrode was incorporated into the cell so that the solution could be pre-electrolyzed without affecting the operating electrode.

The platinum electrodes were prepared by fitting machined lucite plugs to both ends of a re-entrant male ground joint. A $\frac{1}{8}$ in. brass rod threaded into the lucite plug at the solution end passed through a similar plug at the back of the electrode so that the complete assembly could be drawn together with a nut. A platinum disk of appropriate size, punched from a sheet of pure metal and roughened for good adhesion, was pressed to the face of the lucite plug which had been previously softened with a few drops of chloroform. Contact between the platinum and the brass rod was established with a small copper spring. The lucite plug at the solution end was cemented into place with lucite–chloroform solution to prevent electrolyte from leaking in. An apparent area of the platinum face of 0.80 cm.^{2} was the smallest that the design would conveniently permit.

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All electrode surfaces were prepared by grinding with # 225 optical compound (American Optical Co.) and water on a glass surface.

A steady state potential of -0.305 ± 0.005 volt (relative to the saturated calomel electrode) was obtained at a freshly prepared platinum surface within 30 sec. of immersion in oxygen-free $N/5$ sulphuric acid saturated with hydrogen (curve I, Fig. 1, top). The initial potential change, which occurred from

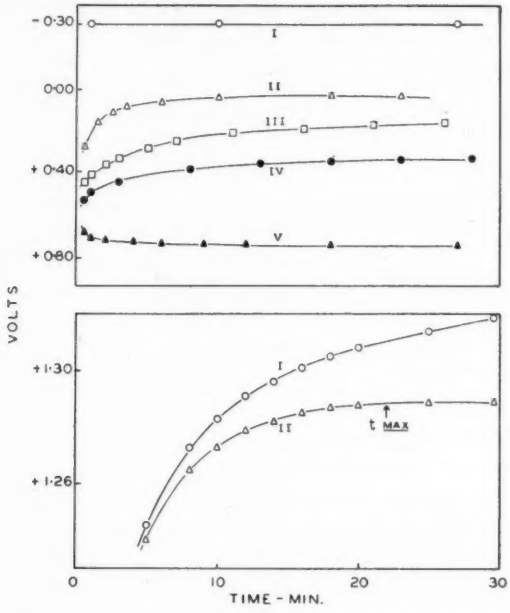


FIG. 1. Top:
Potentials of a platinum electrode in unstirred $N/5$ sulphuric acid electrolyte.
Curve I: Oxygen-free electrolyte, saturated with hydrogen.
II: Oxygen-free electrolyte, saturated with nitrogen.
III: Oxygen concentration approximately 7×10^{-5} molar in nitrogen-saturated electrolyte.
IV: Oxygen concentration approximately 3×10^{-4} molar in nitrogen-saturated electrolyte.
V: Oxygen-saturated electrolyte.
Bottom:
Uncorrected and corrected potential–time curves for a platinum electrode in $N/5$ sulphuric acid electrolyte. Current 1.10×10^{-4} amp.
Curve I: Uncorrected.
II: Corrected.

potentials more positive than -0.30 volt, was much too rapid to follow in detail. When an electrode was immersed in electrolyte saturated with nitrogen, a similar but much less rapid potential change was observed, which reached a value of $+0.05 \pm 0.01$ volt in about 15 min. (curve II, Fig. 1, top) while in oxygen-saturated electrolyte a potential of $+0.745 \pm 0.005$ volt was approached from more negative values (curve V, Fig. 1, top). The potential changed to more positive values when oxygen was introduced into nitrogen-

saturated electrolyte (by electrolysis at an auxiliary platinum electrode) but considerable quantities of oxygen were required to bring about an observable change in the potential curves (curves III and IV, Fig. 1, top). Furthermore, there was no evidence of any definite potential corresponding to some minimum quantity of oxygen as was observed with mercury (II). The platinum electrode potentials in nitrogen-saturated electrolyte containing oxygen were not reproducible and corresponded perhaps to conditions of the electrode surface which depended upon the relative concentrations of oxygen and nitrogen in solution.

The potential difference between a platinum electrode immersed in hydrogen-saturated electrolyte (-0.30 volt) and one immersed in electrolyte saturated with oxygen ($+0.75$ volt) was approximately one volt. These large variations of potential, brought about by changing only the gas dissolved in the electrolyte, would seem to indicate that the observed potentials were the result of some state of the electrode surface involving these gases. The very rapid initial change to a stable and reproducible potential observed when a platinum electrode was immersed in electrolyte saturated with hydrogen would seem to indicate the occurrence of a surface reaction involving very strong forces. This reaction may be the chemisorption of hydrogen. On the other hand, the much slower potential changes observed in solutions containing nitrogen and oxygen indicate surface changes involving much weaker forces. The reactions in these cases may be the strong physical adsorption of molecular oxygen and nitrogen, with oxygen probably the more strongly adsorbed.

When potential build-up curves were established on a mercury cathode (11) in oxygen-free electrolyte saturated with hydrogen (i.e. from initial potentials of about -0.61 volt) two distinct curves were obtained. The initial build-up curve, obtained by passing a small current for the first time across the face of a freshly prepared surface, was nonlinear while the subsequent curve, obtained by allowing the potential to decay on open circuit and again closing the circuit, was linear and reached the steady state potential in a much shorter period of time. In contrast, the initial and subsequent curves on a platinum cathode immersed in hydrogen-saturated solution were identical unless the current was switched on immediately after the electrode was introduced into the electrolyte. However, when the electrolyte was saturated with nitrogen, two distinct build-up curves were obtained as with mercury. The initial curve was now independent of the time of immersion of the electrode prior to switching on the current, provided there was no hydrogen present. In marked contrast with mercury, the initial potential build-up curves on a platinum electrode did not appear to be measurably affected by traces of oxygen.

The time required for the potential to reach a maximum when current was made to flow for the first time across the face of a freshly prepared platinum electrode immersed in $N/5$ sulphuric acid saturated with nitrogen (i.e. t_{max}) was determined for the electrode acting as a cathode and as an anode. With the electrode acting as a cathode, the potential increased smoothly to a maximum after which a slow, almost linear, potential change to more positive values occurred. When the electrode was made anodic, no maximum potential

was observed. After an initial nonlinear curve the potential continued to change to more positive values at a linear rate which was in most cases exactly equal to that following the maximum potential at the cathode. The slow linear potential changes varied between 0.2 and 2 mv./min. depending on the current used, and since they were in the same direction for both anode and cathode, they appeared to be the result of some secondary process for which corrections must be made.

A plot of uncorrected and corrected values for a typical potential build-up curve obtained at a platinum anode is shown in Fig. 1, bottom. The correction, determined from the final approximately linear portion of the curve, is 1 mv./min. Corrections were applied to both anodic and cathodic potential build-up curves and since the final portions of the resultant curves were in all cases very smooth, the values of t_{max} were taken directly from the corrected curves.

The values of t_{max} shown in Table I were obtained by first making the

TABLE I

TYPICAL VALUES OF t_{max} IN $N/5$ SULPHURIC ACID SATURATED WITH NITROGEN

	Zero to anodic		Anodic to cathodic
Current, amp. $\times 10^4$	t_{max}, min.	$t_{max}/2$, min.	t_{max}, min.
4.9	9.2	4.6	3.8
4.6	10.6	5.3	4.8
4.0	9.4	4.7	4.2
3.0	11.6	5.8	6.6
1.9	19.4	9.7	9.0
1.1	12.6	11.3	12.8
0.65	44	22	18
0.53	50	25	24
0.41	64	32	29
0.30	90	45	37

electrode an anode and after t_{max} (anodic) reversing the current so that it became a cathode. For a current range ($4.9 \times 10^{-4} - 0.30 \times 10^{-4}$ amp.) t_{max} for the anode was twice the corresponding value of t_{max} for the cathode. When a freshly prepared electrode was made cathodic and the current was reversed after t_{max}, the value of t_{max} for the anode was approximately three times that for the cathode (Table II). On again reversing the current, t_{max} for the cathode was approximately equal to that observed when the electrode was first made cathodic and was one third of t_{max} observed when the current was reversed after first making the electrode cathodic.

If the quantity of current passed at the cathode in the interval t_{max} is designated one equivalent, then three equivalents are required to establish t_{max} when the current is reversed to make the electrode anodic. Upon again making the electrode cathodic by reversing the current, one equivalent is required to establish t_{max}. A freshly prepared platinum anode requires two equivalents to establish t_{max} (anodic) while as before, t_{max} (cathodic) is established with one equivalent after the current has been reversed.

To explain the foregoing results, it is suggested that:

TABLE II

TYPICAL VALUES OF t_{max} IN $N/5$ SULPHURIC ACID SATURATED WITH NITROGEN

Zero to cathodic	Cathodic to anodic		Anodic to cathodic
t_{max}, min.	t_{max}, min.	$t_{max}/3$, min.	t_{max}, min.
3.9	15.0	5.0	5.6
4.5	15.5	5.2	5.6
3.6	15.6	5.2	5.7
3.3	14.7	4.7	5.2
4.0	15.4	5.1	5.3
3.2	14.5	4.8	5.2
3.9	16.5	5.5	4.8
3.9	15.2	5.1	5.2
Average 3.8		5.1	5.3
Current 2.53×10^{-4} amp.		2.49×10^{-4} amp.	2.53×10^{-4} amp.
Area 230 cm.^{2}		310 cm.^{2}	320 cm.^{2}

Apparent area of electrodes = 0.80 cm.^{2}

1. When a freshly prepared platinum electrode is made cathodic, hydrogen ions are discharged and the atoms adsorbed on the cathode surface in the ratio of one atom of hydrogen to one of platinum until the surface is saturated at the point corresponding to t_{max}.

2. Upon then making the electrode anodic by reversing the current, one equivalent of current is required to remove the film of adsorbed hydrogen and a further two equivalents are required to establish a monatomic film of oxygen in which one atom of oxygen is accommodated by each surface atom of platinum.

3. When a platinum electrode with a freshly prepared surface is made anodic, two equivalents of current are required to deposit a monatomic film of oxygen on the platinum surface in the ratio of one atom of oxygen to one of platinum.

4. Upon now making the electrode cathodic by reversing the current, only one equivalent of current is passed in the interval from t_{max} anodic to t_{max} cathodic. This would seem to indicate that the film of oxygen is displaced from the surface through the reaction $O + O \rightarrow O_2$ (solution), while the hydrogen atoms go directly to the platinum surface.

The values of t_{max} provide a method of calculating the true surface areas of platinum electrodes by the application of Faraday's laws to the quantities of current involved if it is accepted that at t_{max} each surface atom of platinum accommodates one atom of hydrogen at the cathode or one atom of oxygen at the anode. The area occupied by each atom of hydrogen or of oxygen at the surface would then be identical with the effective area of a surface platinum atom. The value of 6.3 Å^2, calculated from bulk density on the assumption that the atoms in solid platinum are close packed, would seem to be a reasonable approximation for the effective area of a platinum atom at the surface.

The areas of platinum electrodes were calculated as above from values of t_{max} representing the average for the eight experiments shown in Table II.

The area calculated from t_{max} (zero to cathodic) was about 27% less than the area calculated from t_{max} (cathodic to anodic) or t_{max} (anodic to cathodic). Thus, when hydrogen is removed from the electrode surface by electrolysis, an actual increase of area appears to take place. Additional evidence for this view would seem to be derived from those experiments which show that a platinum electrode on which the direction of a small current has been reversed between the limits of hydrogen and oxygen evolution becomes very active catalytically (1). An increase of catalytic activity indicates a surface change to some less stable configuration. Such a change could quite conceivably be accompanied by an increase in the true surface area.

Opinions differ concerning the possible existence of a film of hydrogen on an electrode surface when studies are made in which the polarizing current is reversed between the limits of oxygen and hydrogen evolution. Other workers (1, 3–6) have considered only the linear sections of the various potential build-up curves whereas the entire curves have been considered in the present study. The general shapes of the potential build-up curves observed in this study for platinum electrodes are similar to those described by Bowden (1).

The apparent capacitance at cathodes and at anodes of platinum was determined by the method first used successfully by Bowden and Rideal (2). This method involves determination of the rate of potential change with a C.R.O. in the linear portions of the subsequent potential build-up curves. The subsequent curves are obtained after allowing the potential to decay from the initial potential build-up on a freshly prepared electrode.

The apparent capacitance per unit area at the cathode was obtained by dividing the total apparent capacitance, measured in nitrogen-saturated solutions, by the areas calculated from values of t_{max} obtained from both cathodic and anodic initial potential build-up curves (Table III). The apparent

TABLE III

THE APPARENT CAPACITANCE AT A PLATINUM CATHODE IN $N/5$ SULPHURIC ACID SATURATED WITH NITROGEN

Current, amp. $\times 10^4$	A_0, cm.^{2}	A_h, cm.^{2}	Apparent capacitance, microcoulombs/volt	
			Total	Per cm.^{2}
4.9	480	440	43,000	90
4.6	570	530	76,000	140
4.0	410	400	44,000	110
3.0	410	470	42,000	100
1.9	430	410	53,000	130
1.1	290	320	52,000	170
0.65	330	380	38,000	120
0.53	300	300	45,000	150
0.41	300	280	60,000	210
Average				140

Apparent area of cathode = 0.80 cm.^{2}

A_0 = areas calculated by the application of Faraday's laws to values of t_{max} derived from anodic potential build-up curves.

A_h = areas similarly calculated from initial potential build-up curves at the cathode.

TABLE IV

THE APPARENT CAPACITANCE AT A PLATINUM ANODE IN $N/5$ SULPHURIC ACID SATURATED WITH OXYGEN

Current, amp. × 10^4	A_0, cm.^{2}	Apparent capacitance, microcoulombs/volt	
		Total	Per cm.^{2}
2.39	430	2500	5.8
1.19	310	1630	5.3
1.21	340	1800	5.3
1.20	280	1790	6.4
1.19	370	1960	5.3
1.63	380	2010	5.3
1.26	330	1970	6.0
Average			5.6

capacitance per cm.^{2} at the anode was obtained by dividing the total apparent capacitance, measured in oxygen-saturated electrolyte, by the areas calculated from values of t_{max} derived from initial potential build-up curves at the anode (Table IV). The apparent capacitance determined in this way was 140 microcoulombs per volt cm.^{2} at the cathode (average of 10 measurements) and 5.6 microcoulombs per volt cm.^{2} at the anode (average of seven experiments).

The large difference in the apparent capacitance at the cathode and anode would seem to eliminate the possibility that the linear portions of the subsequent build-up curves result from the charging of a Helmholtz double layer of ions in the electrolyte near the electrode surface. A true capacitance from this cause should be approximately equal at both the cathode and anode since the electrolyte was essentially the same in both cases. Although a double layer of ions at the cathode might be expected to differ somewhat from a similar double layer at the anode, it is difficult to rationalize the very large difference of apparent capacitance (which differed by a factor of about 25) on the basis of such a mechanism. It should, perhaps, be borne in mind that the measurement of an apparent capacitance involves the passage of a small current for a period of about one second or less. To establish an appreciable concentration gradient of ions, a similar current would have to be passed for several minutes (9).

Although the electrode behavior of mercury and platinum showed quite substantial differences, these differences appear to be more of degree than of kind. Both metals seem to be capable of accommodating a monatomic film of hydrogen. With mercury this film must be deposited by electrolysis and does not appear to be very stable whereas with platinum a similar film is formed directly from molecular hydrogen in solution and is so adherent that its removal brings about a substantial change in the surface characteristics of the metal. Similarly, both metals appear to be capable of accommodating a monatomic film of oxygen. In this case it is on mercury that such a film is formed from molecular oxygen in solution while on platinum a similar film must be de-

posited by electrolysis. Where conditions are so arranged that these films of hydrogen or of oxygen are formed by electrolysis without appreciable side reactions, they appear to provide a convenient and accurate method of arriving at the true surface area of an electrode.

REFERENCES

1. BOWDEN, F. P. Proc. Roy. Soc. (London), A, 125: 446. 1929.
2. BOWDEN, F. P. and RIDEAL, E. K. Proc. Roy. Soc. (London), A, 120: 59. 1928.
3. BUTLER, J. A. V. and ARMSTRONG, G. Proc. Roy. Soc. (London), A, 137: 604. 1932.
4. BUTLER, J. A. V. and DREVER, G. Trans. Faraday Soc. 32: 427. 1936.
5. HICKLING, A. and TAYLOR, D. Trans. Faraday Soc. 44: 262. 1948.
6. HILSON, P. J. and RIDEAL, E. K. Proc. Roy. Soc. (London), A, 199: 295. 1949.
7. HUTCHEON, A. T. and WINKLER, C. A. Can. J. Research, B, 27: 353. 1949.
8. ROXBURGH, J. M. and WINKLER, C. A. Can. J. Research, B, 28: 383. 1950.
9. TURNER, R. C. and WINKLER, C. A. J. Electrochem. Soc. 99: 78. 1952.
10. WIEBE, A. K., GAUVIN, W., and WINKLER, C. A. Can. J. Chem. 29: 301. 1951.
11. WIEBE, A. K. and WINKLER, C. A. Can. J. Chem. 31: 306. 1953.

CONTRIBUTION TO THE STUDY OF PYRAZOLONES[1]

By Paul E. Gagnon, Jean L. Boivin,[2] and Méüde Tremblay[3]

ABSTRACT

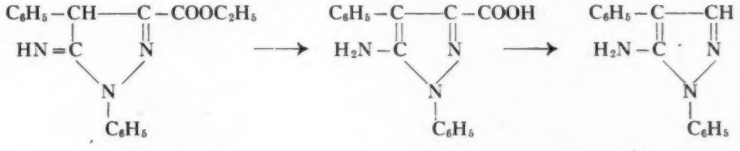
1,4-Diphenyl-3-carbethoxy-5-aminopyrazole yielded 1,4-diphenyl-5-aminopyrazole by hydrolysis and decarboxylation. The phenylhydrazone of ethyl phenyloxalacetate gave a pyrazolone which was transformed into 1,4-diphenyl-3-amino-5-pyrazolone. The 2,4-diphenyl-3-amino-5-pyrazolone was obtained from ethyl phenylcyanoacetate and phenylhydrazine by heating in acetic acid. 4-Alkyl-3-hydroxy- and 3-amino-5-pyrazolones and 4,4-dialkyl-3-oxo- and 3-imino-5-pyrazolones, substituted in position 2 by carbanilino or α- or β-naphthyl groups, were prepared from ethyl mono- or disubstituted malonates and cyanoacetates, 4-phenylsemicarbazide, and α- and β-naphthylhydrazines. Ultraviolet absorption spectra were determined in neutral and acid solutions.

INTRODUCTION

Pyrazolones have been studied extensively for the last few years. For instance, ethyl mono- and disubstituted cyanoacetates with hydrazine and its derivatives gave rise to 5-pyrazolones having amino or imino groups in position 3 (3, 5, 6, 7, 9). Similarly, mono- and disubstituted malonates yielded 5-pyrazolones with hydroxy or oxo groups in position 3 (1, 4).

One of the objects of the present work was to synthesize 1,4- and 2,4-diphenyl-3-amino-5-pyrazolones and determine their structures. Another object was the preparation of 4-alkyl-3-hydroxy and 3-amino-5-pyrazolones and 4,4-dialkyl-3-oxo and 3-imino-5-pyrazolones substituted in position 2 and the determination of their ultraviolet absorption spectra.

1,4-Diphenyl-3-carbethoxy-5-iminopyrazolone (I) (2) was hydrolyzed in order to transform the imino group into an oxo group but the product of the reaction was 1,4-diphenyl-3-carboxy-5-aminopyrazole (II) which yielded 1,4-diphenyl-5-aminopyrazole (III).



I II III

However, by heating together ethyl phenyloxalacetate and phenylhydrazine, 1,4-diphenyl-3-carbethoxy-5-pyrazolone (IV) (10) was obtained. The carbethoxy group in position 3 was hydrolyzed and by decarboxylation a known

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Contribution from the Department of Chemistry, Laval University, Quebec. This paper constitutes part of a thesis submitted to the Graduate School, Laval University, in partial fulfillment of the requirements for the degree of Doctor of Science.

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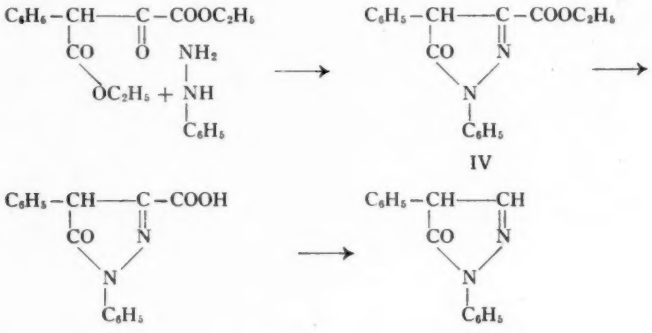
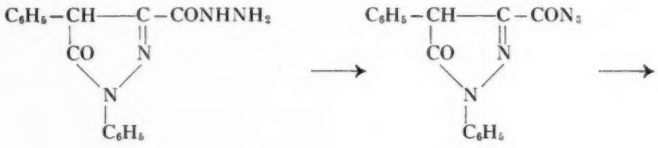
product, 1,4-diphenyl-5-pyrazolone (VI) (12, 13), was formed. This result leaves no doubt as to the constitution of the starting material 1,4-diphenyl-3-carbethoxy-5-pyrazolone (IV).



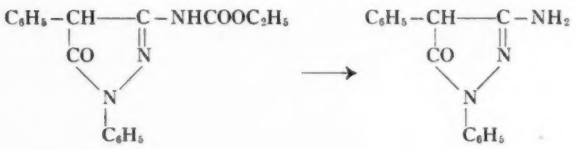
IV

V VI

From 1,4-diphenyl-3-carbethoxy-5-pyrazolone the synthesis of 1,4-diphenyl-3-amino-5-pyrazolone was effected. A Curtius degradation on the 3-carbethoxy group was made through the hydrazide (VII), azide (VIII), and urethane (IX). The alkaline hydrolysis of the urethane yielded 1,4-diphenyl-3-amino-5-pyrazolone (X).

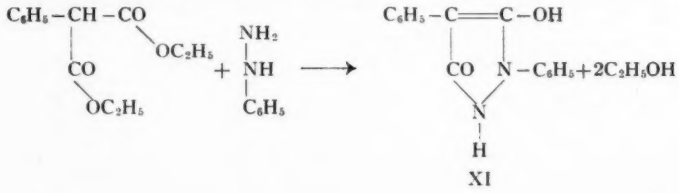


VII VIII



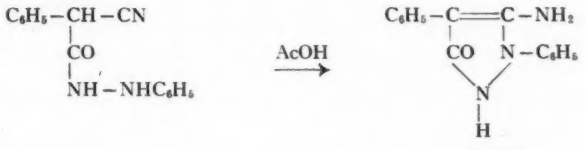
IX X

In order to obtain the 2,4-diphenyl-3-amino-5-pyrazolone, ethyl phenylmalonate was condensed with phenylhydrazine in the presence of sodium ethylate and 2,4-diphenyl-3-hydroxy-5-pyrazolone (XI) was formed.



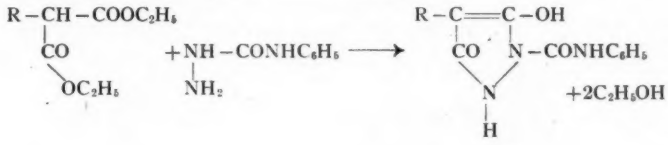
XI

It was intended to use this compound (XI) as starting material and transform the hydroxy group in position 3 into an amino group, but at that time it was found that 2,4-diphenyl-3-amino-5-pyrazolone (XII) could be obtained more easily by heating with acetic acid during many hours the phenylhydrazide of ethyl phenylcyanoacetate (11). All attempts which had previously been made when using sodium ethylate or sodium hydroxide instead of acetic acid had been unsuccessful.



XII

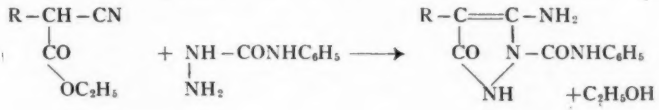
4-Alkyl-3-hydroxy-2-carbanilino-5-pyrazolones (XIII) were prepared according to the method used by Conrad and Zart (1). Ethyl malonates monosubstituted with hexyl, heptyl, or octyl groups were condensed in the presence of sodium ethylate with 4-phenylsemicarbazide.



XIII

With α- or β-naphthylhydrazine hydrochloride under similar conditions, ethyl malonates α-substituted with butyl, amyl, hexyl, heptyl, octyl, or benzyl groups yielded 4-alkyl-3-hydroxy-2-(α or β)-naphthyl-5-pyrazolones (XIV).

4-Monosubstituted-3-amino-2-carbanilino-5-pyrazolones (XV) were obtained from ethyl cyanoacetates α-substituted with butyl, amyl, hexyl, heptyl, octyl, and benzyl groups also in the presence of sodium ethylate.



XV

4,4-Dialkyl-3-oxo-2-carbanilino-5-pyrazolones (XVI) were prepared from ethyl malonates disubstituted with butyl, hexyl, heptyl, octyl, and benzyl groups and 4-phenylsemicarbazide.

Ethyl dibenzylmalonate and β-naphthylhydrazine hydrochloride gave 4,4-dibenzyl-3-oxo-2-β-naphthyl-5-pyrazolone (XVII) under the same experimental conditions.

Ethyl cyanoacetates disubstituted with butyl, amyl, hexyl, and octyl groups were heated under reflux with sodium ethylate and 4-phenylsemicarbazide to yield 4,4-dialkyl-3-imino-2-carbanilino-5-pyrazolones (XVIII).

TABLE I

4-PHENYL-5-PYRAZOLONES

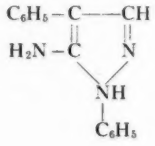
Substituents			Formula	M.p., °C.	Analysis		Ultraviolet absorption maxima			
					Nitrogen, %		Neutral		Acid	
3	2	1			Calc.	Found	Å	Log E_m	Å	Log E_m
$COOC_2H_5$		C_6H_5	$C_{18}H_{16}O_3N_2$	142–143	9.09	8.77	2410	4.32	2450	4.27
COOH		C_6H_5	$C_{16}H_{12}O_3N_2$	192–193	10.00	9.53	2440	4.40	2450	4.34
		C_6H_5	$C_{15}H_{12}ON_2$	196–197	11.75	11.4	2550 2830	4.34 4.18	2440	4.16
$CONHNH_2$		C_6H_5	$C_{16}H_{14}O_2N_4$	203–204	19.04	18.9	2400	4.50	2420	4.52
$NHCOOC_2H_5$		C_6H_5	$C_{18}H_{17}O_3N_3$	193–194	13.00	13.0	2520 3050	4.31 3.50	2510 2980	4.38 3.49
NH_2		C_6H_5	$C_{15}H_{13}ON_3$	153–156d	16.73	15.9	2560	4.26	2540	4.20
OH	C_6H_5		$C_{15}H_{12}O_2N_2$	172–173	11.11	11.6	2350 2820	4.18 3.30	2340 2800	4.16 3.31
NH_2	C_6H_5		$C_{15}H_{13}ON_3$	234–236	16.73	16.0	2800	4.26	2500	4.18

The properties and analysis of the pyrazolones are given in Tables I, II, III, and IV.

Ultraviolet Absorption Spectra

The ultraviolet absorption spectra were determined in neutral and acid solution by a method already described (7).

1,4-Diphenyl-5-aminopyrazole (Fig. 1) has a single ultraviolet absorption maximum of high intensity, log E_m = 4.31, at short wave length, 2490 Å in neutral medium. On acidification, the maximum is shifted to shorter wave length. It has been shown that pyrazolones with a low absorption maximum at high wave length have a 2:3 double bond or an imino group, and that those with a high maximum at short wave length have a double bond between two carbon atoms (3, 6, 7). Moreover, the hypsochromic shift was attributed to the formation of a salt by an amino group (11). From these results one may be justified to conclude that structure XIX is the only one present.



XIX

1,4-Diphenyl-3-amino-5-pyrazolone (Fig. 2) has only one ultraviolet absorption maximum of high intensity at short wave length either in neutral or

TABLE II

3-HYDROXY-5-PYRAZOLONES

Substituents		Formula	M.p., °C.	Analysis		Ultraviolet absorption maxima			
				Nitrogen, %		Neutral		Acid	
4	2			Calc.	Found	Å	Log E_m	Å	Log E_m
C_6H_{13}	$CONHC_6H_5$	$C_{16}H_{21}O_3N_3$	170–171 dec.	13.86	13.7	2380	4.05	2370	3.99
C_7H_{15}	$CONHC_6H_5$	$C_{17}H_{23}O_3N_3$	160–162 dec.	13.28	13.6	2380	4.20	2380	4.10
C_8H_{17}	$CONHC_6H_5$	$C_{18}H_{25}O_3N_3$	150–151	12.69	13.5	2540	4.37	2540	4.38
C_8H_{17}	α-$C_{10}H_7$	$C_{21}H_{26}O_2N_2$	184–185	8.28	7.97	2400 3140	4.32 3.74	2380 3050	4.29 3.74
$C_6H_5CH_2$	α-$C_{10}H_7$	$C_{20}H_{16}O_2N_2$	169–170	8.86	8.54	2230 2770	4.76 3.88	2235 2810	4.71 3.94
C_4H_9	β-$C_{10}H_7$	$C_{17}H_{18}O_2N_2$	172–173	9.93	10.0	2440 2975	4.45 4.28	2320 3010	4.67 3.90
C_5H_{11}	β-$C_{10}H_7$	$C_{18}H_{20}O_2N_2$	157–158	9.46	9.32	2440 2980	4.47 4.01	2330 2940	4.61 3.92
C_6H_{13}	β-$C_{10}H_7$	$C_{19}H_{22}O_2N_2$	155–156	9.03	8.67	2270 2890	4.54 3.92	2310 3000	4.61 3.90
C_7H_{15}	β-$C_{10}H_7$	$C_{20}H_{24}O_2N_2$	152–153	8.64	8.79	2450 3000	4.45 4.00	2320 2990	4.52 3.88
C_8H_{17}	β-$C_{10}H_7$	$C_{21}H_{26}O_2N_2$	147–148	8.28	8.02	 3000	 3.97	2340 3000	4.61 3.89
$C_6H_5CH_2$	β-$C_{10}H_7$	$C_{20}H_{16}O_2N_2$	189–190	8.86	8.80	2350 3000	4.53 3.75	 3000	 3.79

TABLE III

3-AMINO-2-CARBANILINO-5-PYRAZOLONES

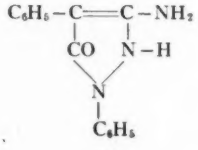
Substituents	Formula	M.p., °C.	Analysis		Ultraviolet absorption maxima			
			Nitrogen, %		Neutral		Acid	
4			Calc.	Found	Å	Log E_m	Å	Log E_m
C_4H_9	$C_{14}H_{18}O_2N_2$	117–118	20.43	20.3	2380	4.22	2420	4.30
C_5H_{11}	$C_{15}H_{20}O_2N_4$	115–116	19.44	19.4	2480	4.34	2380	4.24
C_6H_{13}	$C_{16}H_{22}O_2N_4$	113–114	18.54	17.9	2420	4.50	2370	4.22
C_7H_{15}	$C_{17}H_{24}O_2N_4$	110–111	17.72	17.8	2450	4.33	2400	4.28
C_8H_{17}	$C_{18}H_{26}O_2N_4$	264–265	16.97	16.8	2460 2920	4.18 3.68	2430 2840	4.30 3.77
$C_6H_5CH_2$	$C_{17}H_{16}O_2N_4$	240–245	18.18	17.5	2880	3.79	2790	3.73

TABLE IV

4,4-DIALKYL-5-PYRAZOLONES

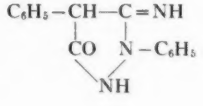
Substituents			Formula	M.p., °C.	Analysis		Ultraviolet absorption maxima			
					Nitrogen, %		Neutral		Acid	
4	3	2			Calc.	Found	Å	log E_m	Å	log E_m
$(C_4H_9)_2$	O	$CONHC_6H_5$	$C_{18}H_{25}O_2N_3$	217–218	12.68	12.9	2550	3.74	2520	3.81
$(C_6H_{13})_2$	O	$CONHC_6H_5$	$C_{22}H_{33}O_2N_3$	198–199	10.85	10.8	2530	3.74	2510	3.77
$(C_7H_{15})_2$	O	$CONHC_6H_5$	$C_{24}H_{37}O_2N_3$	199–200	10.12	10.3	2510	3.72	2450	3.83
(C_8H_{17})	O	$CONHC_6H_5$	$C_{26}H_{41}O_2N_3$	194–195	9.48	9.50	2530	3.69	2520	3.75
$(C_6H_5CH_2)_2$	O	$CONHC_6H_5$	$C_{24}H_{21}O_2N_3$	243–245	10.52	10.6	2400	3.39	2400	4.41
$(C_6H_5CH_2)_2$	O	β-$C_{10}H_7$	$C_{24}H_{22}O_2N_2$	243–244	6.89	6.42	2990	3.89	2970	3.89
$(C_4H_9)_2$	NH	$CONHC_6H_5$	$C_{18}H_{26}O_2N_4$	234–236	16.97	17.3				
$(C_5H_{11})_2$	NH	$CONHC_6H_5$	$C_{20}H_{30}O_2N_4$	95–97	15.64	15.9	2460	4.48	2400	4.25
$(C_6H_{13})_2$	NH	$CONHC_6H_5$	$C_{22}H_{34}O_2N_4$	100–102	14.51	14.9	2450	4.54	2380	4.15
$(C_8H_{17})_2$	NH	$CONHC_6H_5$	$C_{26}H_{42}O_2N_4$	167–168	12.67	13.4	2700	3.82	2660	3.89

acid solution, which is indicative of the presence of a 3:4 ethylenic double bond as shown by formula XX.

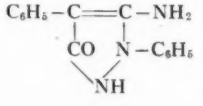


XX

2,4-Diphenyl-3-amino-5-pyrazolone (Fig. 2) has an absorption maximum at long wave length in neutral medium and this suggests that form XXI is present. But in acid solution a comparison of the curve of the 2,4 with that of the 1,4-diphenyl-3-amino-5-pyrazolone reveals that form XXII then exists.



XXI



XXII

4-Monosubstituted-3-hydroxy-2-carbanilino-5-pyrazolones (R = C_6H_{13}, C_7H_{15}, or C_8H_{17}) exhibit only one absorption band in neutral or acid solution at short wave length (Fig. 3) which is indicative of an ethylenic bond (4). They may have the structures XXIII or XXIV.

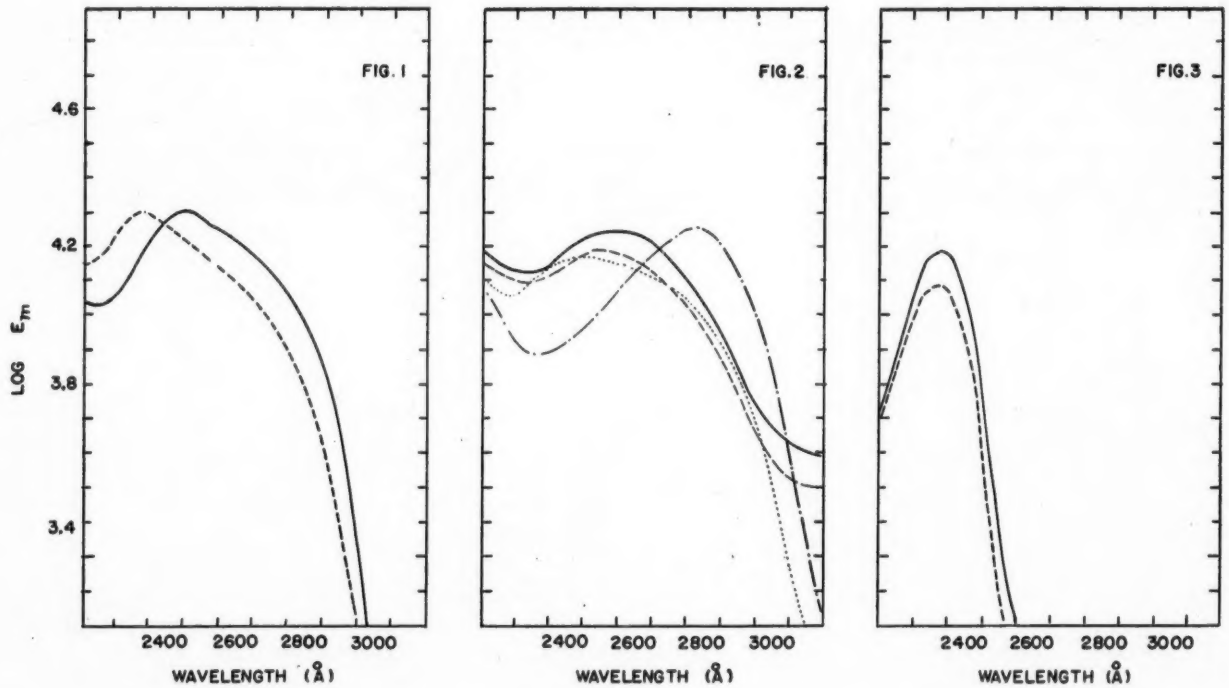


FIG. 1. Ultraviolet absorption spectrum of 1,4-diphenyl-5-aminopyrazole: ———— in neutral solution, – – – – – in acid solution.
FIG. 2. Ultraviolet absorption spectrum of 1,4-diphenyl-3-amino-5-pyrazolone: ———— in neutral solution, – – – – – in acid solution; and of 2,4-diphenyl-3-amino-5-pyrazolone: – · – · – · – in neutral solution, ... in acid solution.
FIG. 3. Ultraviolet absorption spectrum of 4-heptyl-3-hydroxy-2-carbanilino-5-pyrazolone: ———— in neutral solution, – – – – – in acid solution.

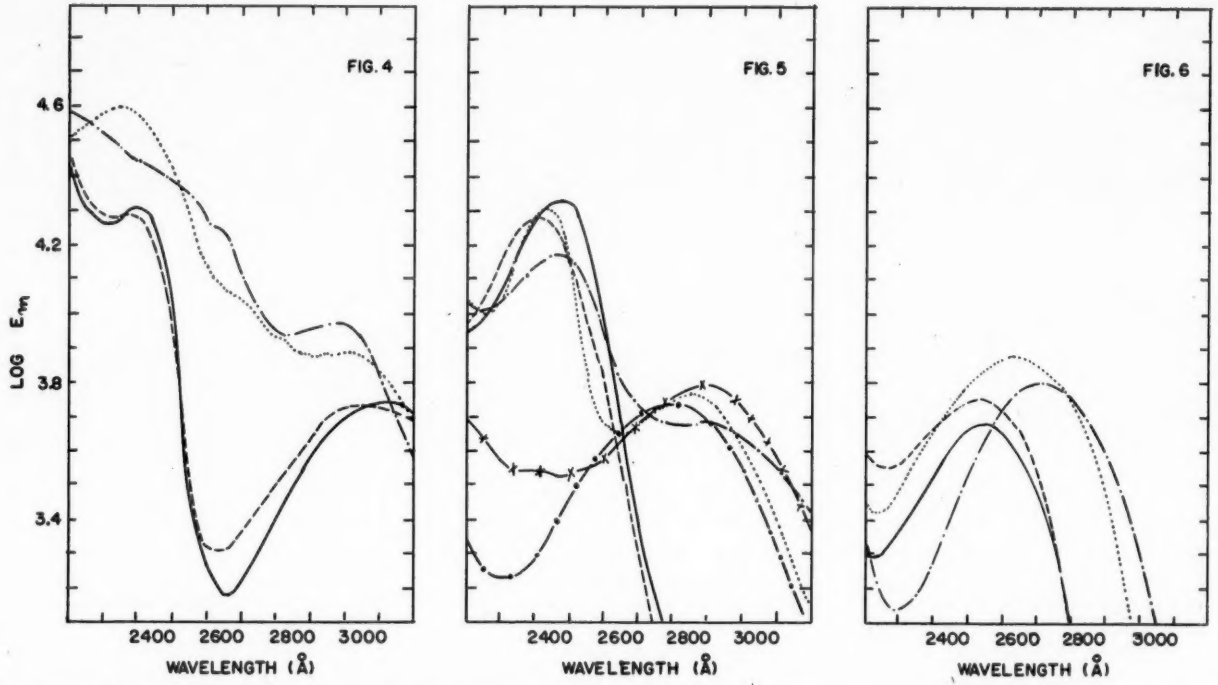
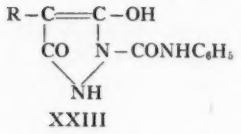


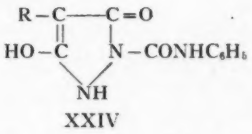
FIG. 4. Ultraviolet absorption spectrum of 4-octyl-3-hydroxy-2-α-naphthyl-5-pyrazolone: ———— in neutral solution, – – – – – in acid solution; and of 4-octyl-3-hydroxy-2-β-naphthyl-5-pyrazolone: – · – · – · – in neutral solution, ... in acid solution.

FIG. 5. Ultraviolet absorption spectrum of 4-heptyl-3-amino-2-carbanilino-5-pyrazolone: ———— in neutral solution, – – – – – in acid solution; of 4-octyl-3-amino-2-carbanilino-5-pyrazolone: – · – · – · – in neutral solution, ... in acid solution; and of 4-benzyl-3-amino-2-carbanilino-5-pyrazolone: – x – x – x – in neutral solution, – • – • – • – • – in acid solution.

FIG. 6. Ultraviolet absorption spectrum of 4,4-dioctyl-3-oxo-2-carbanilino-5-pyrazolone: ———— in neutral solution, – – – – – in acid solution; and of 4,4-dioctyl-3-imino-2-carbanilino-5-pyrazolone: – · – · – · – in neutral solution, ... in acid solution.



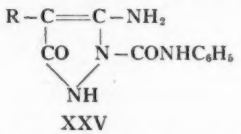
XXIII



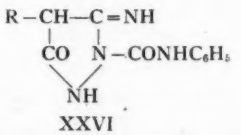
XXIV

The spectra of 4-monosubstituted-3-hydroxy-2-α-naphthyl-5-pyrazolones (R = C_8H_{17} or $C_6H_5CH_2$) and 4-monosubstituted-3-hydroxy-2-β-naphthyl-5-pyrazolones (R = C_4H_9, C_5H_{11}, C_6H_{13}, C_7H_{15}, C_8H_{17}, or $C_6H_5CH_2$) (Fig. 4) are greatly influenced by the absorption of the naphthalene chromophore (3, 8). However, these pyrazolones probably have structures similar to the previous ones XXIII or XXIV.

The absorption curves of most of the 4-alkyl-3-amino-2-carbanilino-5-pyrazolones (R = C_4H_9, C_5H_{11}, C_6H_{13}, or C_7H_{15}) (Fig. 5) exhibit in neutral and acid solution only one maximum of high intensity at short wave length. This fact together with the slight shift on acidification indicates the presence of an amino group as in structure XXV.



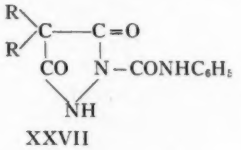
XXV



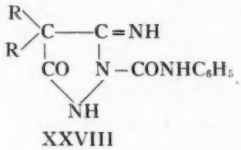
XXVI

On the other hand 4-octyl-3-amino-2-carbanilino-5-pyrazolones (Fig. 5) have two ultraviolet absorption maxima in neutral and acid solution, one at short wave length and one at long wave length. One must conclude that two forms, one with an amino group in position 3, structure XXV, and another with an imino group XXVI, are present. 4-Benzyl-3-amino-2-carbanilino-5-pyrazolone (Fig. 5) has only one maximum at long wave length and consequently has structure XXVI.

4,4-Dialkyl-3-oxo-2-carbanilino-5-pyrazolones (R = C_4H_9, C_6H_{13}, C_7H_{15}, C_8H_{17}, or $C_6H_5CH_2$) and 4,4-dialkyl-3-imino-2-carbanilino-5-pyrazolones (R = C_4H_9, C_5H_{11}, C_6H_{13}, or C_8H_{17}) (Fig. 6) certainly have structures XXVII and XXVIII in neutral and acid solution since they are the only ones possible.



XXVII



XXVIII

EXPERIMENTAL*

1,4-Diphenyl-3-carboxy-5-aminopyrazole (II)

To 1,4-diphenyl-3-carbethoxy-5-aminopyrazole (2) (1.0 gm., 0.003 mole) was added sodium hydroxide (10%, 50 ml.) in absolute alcohol (25 ml.). The mixture was heated under reflux for three hours and the solution was poured into ice water. On neutralization with dilute acetic acid the starting material

* *All melting points are uncorrected.*

was obtained and removed by filtration. By acidification to pH 3 with hydrochloric acid, a white solid precipitated. This compound was recrystallized from alcohol: m.p. 109–110° C. Yield, 0.5 gm. (60%). Calc. for $C_{16}H_{13}O_2N_3$: N, 15.05%. Found: N, 14.7%.

1,4-Diphenyl-5-aminopyrazole (III)

1,4-Diphenyl-3-carboxy-5-aminopyrazole (1.1 gm., 0.004 mole) was heated at 200° C. for 45 min., until all the carbon dioxide had been expelled. The cold solid residue was recrystallized from ethanol: m.p. 136–137° C. Yield, 0.3 gm. (32%). Calc. for $C_{15}H_{13}N_3$: N, 17.87%. Found: N, 17.3%.

1,4-Diphenyl-3-carbethoxy-5-pyrazolone (IV)

Ethyl phenyloxalacetate (33.5 gm., 0.127 mole) was mixed with phenylhydrazine (10.8 gm., 0.1 mole) and the mixture was heated on a steam bath for an hour and in an oil bath at 210° C. for two hours. The material was dissolved in alcohol and the solution poured into dilute alkali. The alkaline solution was filtered and the filtrate was acidified with acetic acid. The product (10) was recrystallized from dilute alcohol: m.p. 142–143° C. Yield, 18 gm. (50%). Calc. for $C_{18}H_{16}O_3N_2$: N, 9.09%. Found: N, 8.77%.

1,4-Diphenyl-3-carboxy-5-pyrazolone (V)

1,4-Diphenyl-3-carbethoxy-5-pyrazolone (4.0 gm., 0.013 mole) was heated on a steam bath with alcoholic potash for one hour. The product was poured into ice water and the solution treated with an excess of hydrochloric acid (50%). The white precipitate that separated was recrystallized from chloroform: m.p. 192–193° C. Calc. for $C_{16}H_{12}O_3N_2$: N, 10.00%. Found: N, 9.53%.

1,4-Diphenyl-5-pyrazolone (VI)

1,4-Diphenyl-3-carboxy-5-pyrazolone was heated in a metal bath at 200° C. for 30 min. The solid residue (12, 13) was recrystallized from ethanol: m.p. 196–197° C. Calc. for $C_{15}H_{12}ON_2$: N, 11.75%. Found: N, 11.4%.

1,4-Diphenyl-3-carboxyhydrazido-5-pyrazolone (VII)

1,4-Diphenyl-3-carbethoxy-5-pyrazolone (7.7 gm., 0.025 mole) was added to boiling hydrazine hydrate (100%, 10 ml.). The mixture was refluxed for six hours and evaporated to dryness. The residue was dissolved in cold hydrochloric acid and poured into ice water. On neutralization with sodium hydroxide, a solid separated and was recrystallized from alcohol: m.p. 203–204° C. Calc. for $C_{16}H_{14}O_2N_4$: N, 19.04%. Found: N, 18.9%.

1,4-Diphenyl-3-carbethoxyamino-5-pyrazolone (IX)

A solution of 1,4-diphenyl-3-carboxyhydrazido-5-pyrazolone in hydrochloric acid was cooled to 0° C. and covered with ether. Sodium nitrite dissolved in water was added dropwise to the mechanically stirred mixture until the diazotization was complete, as shown by the starch–iodide test paper. The ethereal layer was decanted and the aqueous solution extracted several times with ether. The extracts were washed with sodium bicarbonate (10%), dried over anhydrous sodium sulphate, and evaporated to dryness under reduced pressure.

The solid product, the azide melting at about 160° C. (with deflagration), was dissolved in absolute ethanol and the solution was refluxed for 20 hr. A white solid material separated: m.p. 193–194° C. The urethane was sublimed at 180° C. (1 mm.). Calc. for $C_{18}H_{17}O_3N_3$: N, 13.00%. Found: N, 13.0%.

1,4-Diphenyl-3-amino-5-pyrazolone (X)

1,4-Diphenyl-3-carbethoxyamino-5-pyrazolone (0.6 gm.) was treated with dilute (10%) sodium hydroxide and the mixture was refluxed for three hours, cooled, filtered, and acidified with dilute (50%) acetic acid. The brown precipitate formed was dissolved in absolute ether. The ethereal solution was dried over anhydrous sodium sulphate, evaporated to dryness, and the solid residue was recrystallized from benzene: m.p. 153–156° C. (with decomposition). The product decomposed at 140° C. (1 mm.) in an attempt to sublime it. Calc. for $C_{15}H_{13}ON_3$: N, 16.73%. Found: 15.9%.

2,4-Diphenyl-3-hydroxy-5-pyrazolone (XI)

Ethyl phenylmalonate (11.8 gm., 0.05 mole) and phenylhydrazine (5.4 gm., 0.05 mole) were added to a cold solution of sodium (2.4 gm., 0.1 mole) in absolute ethanol (75 ml.). The solution was refluxed for 18 hr., the alcohol was evaporated under reduced pressure, and the residue dissolved in water. The water insoluble material was recrystallized from alcohol: m.p. 172–173° C. Yield, 9 gm. (70%). Calc. for $C_{15}H_{12}O_2N_2$: N, 11.11%. Found: 11.6%.

2,4-Diphenyl-3-amino-5-pyrazolone (XII)

The phenylhydrazine derivative of ethyl phenylcyanoacetate (4.2 gm., 0.017 mole) (11) was dissolved in boiling glacial acetic acid (50 ml.) and the solution refluxed for 72 hr. On cooling, a solid crystallized and was dissolved in a cold sodium hydroxide solution (5%, 400 ml.). The alkaline solution was filtered, some insoluble materials were thus removed, and the filtrate was acidified with acetic acid. The white precipitate was recrystallized from ethanol: m.p. 234–236° C. Yield, 2.0 gm. (47%). Calc. for $C_{15}H_{13}ON_3$: N, 16.73%. Found: N, 16.0%.

4-Monosubstituted-3-hydroxy-5-pyrazolone (XIII and XIV)

Mixtures of ethyl monosubstituted malonates (0.033 mole) and hydrazine derivatives, 4-phenylsemicarbazide or α- or β-naphthylhydrazine hydrochloride (0.033 mole) were added to cold solutions of sodium (0.10 mole) in absolute ethanol (75 ml.). After the solutions were refluxed for 18 hr., the alcohol was evaporated under reduced pressure and the residues dissolved in water. The solutions were extracted with ether, filtered to remove the insoluble material, and the aqueous layers were acidified with acetic acid (50%). Solids separated and were recrystallized with ethanol. Some of them were sublimed under reduced pressure (1 mm.) at 10° C. below their melting points.

The 4-monosubstituted-3-hydroxy-5-pyrazolones obtained are listed together with their melting points, analyses, and ultraviolet spectrophotometric data in Table II.

4-Monosubstituted-3-amino-2-carbanilino-5-pyrazolones (XV)

The 4-monosubstituted-3-amino-2-carbanilino-5-pyrazolones were prepared

in the same way as above, except that the ethyl monosubstituted malonates used were replaced by ethyl monosubstituted cyanoacetates.

They are listed together with their melting points, analyses, and ultraviolet spectrophotomeric data in Table III.

4,4-Disubstituted-3-oxo-5-pyrazolones (XVI and XVII)

Using the same procedure as outlined for 4-monosubstituted-3-hydroxy-5-pyrazolones, 4,4-disubstituted-3-oxo-5-pyrazolones were obtained from ethyl disubstituted malonates and 4-phenylsemicarbazide or β-naphthylhydrazine hydrochloride and their melting points, analyses, and ultraviolet spectrophotometric data are listed in Table IV.

4,4-Disubstituted-3-imino-2-carbanilino-5-pyrazolones (XVIII)

Ethyl dialkyl cyanoacetates were treated with 4-phenylsemicarbazide just as indicated for 4-alkyl-3-hydroxy-5-pyrazolones to yield 4,4-dialkyl-3-imino-2-carbanilino-5-pyrazolones.

Their properties are summarized in Table IV.

REFERENCES

1. CONRAD, M. and ZART, A. Ber. 39: 2882. 1906.
2. ERLENMEYER, E. Ber. 33: 2592. 1887.
3. GAGNON, P. E., BOIVIN, J. L., and BOIVIN, P. A. Can. J. Research, B, 28: 720. 1950.
4. GAGNON, P. E., BOIVIN, J. L., and BOIVIN, P. A. Can. J. Chem. 29: 182. 1951.
5. GAGNON, P. E., BOIVIN, J. L., BOIVIN, P. A., and CRAIG, H. M. Can. J. Chem. 30: 52. 1952.
6. GAGNON, P. E., BOIVIN, J. L., and CHISHOLM, A. Can. J. Chem. 30: 904. 1952.
7. GAGNON, P. E., BOIVIN, J. L., and JONES, R. N. Can. J. Research, B, 27: 190. 1949.
8. GAGNON, P. E., NOLIN, B., and JONES, R. N. Can. J. Chem. 29: 843. 1951.
9. GAGNON, P. E., SAVARD, K., GAUDRY, R., and RICHARDSON, E. D. Can. J. Research, B, 25: 28. 1947.
10. GEIGY, J. R. Brit. Patent, 563, 279. Aug. 8, 1944.
11. HESSLER, J. C. Am. Chem. J. 39: 63. 1908.
12. WISLICENUS, W. Ber. 20: 2932. 1887.
13. WISLICENUS, W. Ber. 28: 773. 1895.

CHARACTERIZATION OF DINITROALKYL PHENOLS[1]

By G. G. S. Dutton, T. I. Briggs,[2] B. R. Brown,[3] and M. E. D. Hillman

ABSTRACT

Amine salts of dinitroalkyl phenols have been suggested as herbicides and insecticides. A selection of such amine salts was examined as to their suitability for characterizing dinitroalkyl phenols. The following new salts are described: the piperidine, morpholine, and cyclohexylamine salts of each of 2,4-dinitrophenol, 4,6-dinitro-2-methylphenol, 2,6-dinitro-4-methylphenol, 4,6-dinitro-2-isopropylphenol, 2,6-dinitro-4-isopropylphenol, 4,6-dinitro-2-(*sec*-butyl)-phenol, 2,6-dinitro-4-(*tert*-butyl)-phenol, and 2,6-dinitro-4-(*tert*-amyl)-phenol. In addition, the preparation of 4,6-dinitro-2-isopropylphenol and 2,6-dinitro-4-isopropylphenol does not appear to have been previously described. The use of these salts, and similar ones with other amines, is recommended for the preparation of crystalline derivatives of dinitrophenols.

INTRODUCTION

Dinitroalkyl phenols have been shown to be effective as insecticides (2, 3) and selective weed killers (6). In connection with a study of such compounds as herbicides a selection of dinitroalkyl phenols has been prepared. The amine salts of these dinitroalkyl phenols were prepared and were found to be excellent derivatives for the characterization of these compounds.

The reported method of preparing such amine salts (4) (sodium salt of phenol + amine hydrochloride) has given in our hands crystalline mixtures of the phenol and the desired salt. The discrepancies between the reported melting points of some of these salts (4) and those described here are attributed to this cause. Bell's melting point (1) of 171° C. for piperidinium 2,4-dinitrophenoxide agrees well with our figure of 172° C.

EXPERIMENTAL

The phenols selected for nitration were 2-and 4-methylphenol, 2- and 4-isopropylphenol, 4-(*tert*-butyl)-phenol, and 4-(*tert*-amyl)-phenol. The latter two were prepared by the method of Putnam (5) and the remainder, together with 2,4-dinitrophenol and 2,4-dinitro-2-(*sec*-butyl)-phenol, were obtained as commercial products.

4,6-Dinitro-2-isopropylphenol

2-Isopropylphenol (25 gm.) was dissolved in glacial acetic acid (60 cc.) and this solution was added dropwise, with constant stirring, to a solution of nitric acid (40 cc., $d = 1.5$) and glacial acetic acid (75 cc.) which had been cooled to −15° C. in a stainless steel beaker. The addition took about three quarters of an hour, after which time the mixture was allowed to come slowly to room temperature over a period of one and a half hours. The solution was kept at room temperature for one half hour and then poured onto cracked ice.

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Contribution from the Department of Chemistry, University of British Columbia, Vancouver 8, B.C.
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The yellow precipitate which resulted was filtered off, dissolved in chloroform, and carefully washed to remove all trace of acid. The chloroform solution was then dried over magnesium sulphate and after removal of the solvent, the residual oil was distilled under high vacuum to give the 4,6-dinitro-2-isopropylphenol as a clear yellow oil boiling at 132° C. (0.15 mm.). The oil solidified on cooling and on recrystallization from ethanol gave a yellow solid, m.p. 54° C., yield, 65%.

In a similar manner all the other dinitrophenols were prepared and the results shown in Table I.

TABLE I

DINITROALKYL PHENOLS

Phenol	M.p., °C.	Yield, %
2,4-Dinitro	114	*
4,6-Dinitro-2-methyl	86	67
2,6-Dinitro-4-methyl	82	60
4,6-Dinitro-2-isopropyl	54	66
2,6-Dinitro-4-isopropyl	68	65
4,6-Dinitro-2-(*sec*-butyl)	42	*
2,6-Dinitro-4-(*tert*-butyl)	95	80
2,6-Dinitro-4-(*tert*-amyl)	66	50

**Commercial sample.*

Piperidine Salt of 4,6-Dinitro-2-methylphenol

4,6-Dinitro-2-methylphenol (0.5 gm.) was placed in an Erlenmeyer flask and a small excess of piperidine (0.75 gm.) was added. Benzene (10 cc.) was then added and the mixture gently warmed for five minutes. Petroleum ether (25 cc., 30–60° C.) was then added when the salt crystallized as colored flakes. The precipitate was filtered off, washed with petroleum ether, and recrystallized from a mixture of benzene (five parts), ethanol (one part), and petroleum ether (two parts).

In a similar way the piperidine, morpholine, and cyclohexylamine salts of all the dinitrophenols were prepared and these are listed in Tables II, III, and IV.

TABLE II

PIPERIDINE SALTS OF DINITROALKYL PHENOLS

Phenol	Formula	M.p., °C.	Nitrogen, %		Description
			Calc.	Found	
2,4-Dinitro	$C_{11}H_{15}N_3O_5$	172*	15.61	15.54	Orange needles
4,6-Dinitro-2-methyl	$C_{12}H_{17}N_3O_5$	157	14.83	14.93	Yellow needles
2,6-Dinitro-4-methyl	$C_{12}H_{17}N_3O_5$	195	14.83	14.86	Orange needles
4,6-Dinitro-2-isopropyl	$C_{14}H_{21}N_3O_5$	204	13.50	13.52	Yellow needles
2,6-Dinitro-4-isopropyl	$C_{14}H_{21}N_3O_5$	218	13.50	13.44	Orange plates
4,6-Dinitro-2-(*sec*-butyl)	$C_{15}H_{23}N_3O_5$	154	12.92	12.93	Yellow needles
2,6-Dinitro-4-(*tert*-butyl)	$C_{15}H_{23}N_3O_5$	232	12.92	12.92	Orange needles
2,6-Dinitro-4-(*tert*-amyl)	$C_{16}H_{25}N_3O_5$	198	12.39	12.54	Orange plates

* *Ref.(1).*

TABLE III

MORPHOLINE SALTS OF DINITROALKYL PHENOLS

Phenol	Formula	M.p., °C.	Nitrogen, %		Description
			Calc.	Found	
2,4-Dinitro	$C_{10}H_{13}N_3O_6$	169	15.49	15.36	Yellow needles
4,6-Dinitro-2-methyl	$C_{11}H_{15}N_3O_6$	189	14.74	14.76	Red plates
2,6-Dinitro-4-methyl	$C_{11}H_{15}N_3O_6$	217	14.74	14.73	Orange plates
4,6-Dinitro-2-isopropyl	$C_{13}H_{19}N_3O_6$	204	13.42	13.54	Orange needles
2,6-Dinitro-4-isopropyl	$C_{13}H_{19}N_3O_6$	216	13.42	13.55	Yellow flakes
4,6-Dinitro-2-(*sec*-butyl)	$C_{14}H_{21}N_3O_6$	147	12.84	12.89	Red needles
2,6-Dinitro-4-(*tert*-butyl)	$C_{14}H_{21}N_3O_6$	232	12.84	12.92	Orange needles
2,6-Dinitro-4-(*tert*-amyl)	$C_{15}H_{23}N_3O_6$	174	12.32	12.22	Yellow plates

TABLE IV

CYCLOHEXYLAMINE SALTS OF DINITROALKYL PHENOLS

Phenol	Formula	M.p., °C.	Nitrogen, %		Description
			Calc.	Found	
2,4-Dinitro	$C_{12}H_{17}N_3O_6$	158	14.83	14.85	Yellow needles
4,6-Dinitro-2-methyl	$C_{13}H_{19}N_3O_6$	171	14.13	14.23	Yellow needles
2,6-Dinitro-4-methyl	$C_{13}H_{19}N_3O_6$	193	14.13	14.16	Orange needles
4,6-Dinitro-2-isopropyl	$C_{15}H_{23}N_3O_6$	207	12.92	12.95	Yellow needles
2,6-Dinitro-4-isopropyl	$C_{15}H_{23}N_3O_6$	213	12.92	12.99	Orange needles
4,6-Dinitro-2-(*sec*-butyl)	$C_{16}H_{25}N_3O_6$	210	12.38	12.44	Yellow needles
2,6-Dinitro-4-(*tert*-butyl)	$C_{16}H_{25}N_3O_6$	230	12.38	12.39	Orange needles
2,6-Dinitro-4-(*tert*-amyl)	$C_{17}H_{27}N_3O_6$	219	11.90	11.93	Yellow needles

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REFERENCES

1. BELL, F. J. Chem. Soc. 609. 1931.
2. CRAFTS, A. S. Science, 101: 417. 1945.
3. KAGY, J. F. J. Econ. Entomol. 34: 660. 1941.
4. MIGRDICHIAN, V. U.S. Pat. No. 2,385,719. 1945.
5. PUTNAM, M. E. U.S. Pat. No. 2,039,044. 1936.
6. WESTGATE, W. A. and RAYNOR, R. N. Calif. Dept. Agr. Bull. No. 634. 1940.

STEROIDS

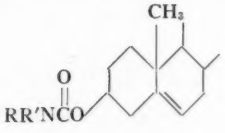
II. REACTION OF AMINES WITH CHOLESTERYL CHLOROFORMATE AND PYROLYSIS OF N-BENZYL CHOLESTERYL CARBAMATE[1]

By A. F. McKay and G. R. Vavasour

ABSTRACT

Cholesteryl chloroformate can be used to isolate small amounts of amines from aqueous solutions as N-substituted cholesteryl carbamates. These derivatives are easily isolated and identified. Their possible use for the identification of amines obtained in degradative studies is discussed. The thermal decomposition of N-benzyl cholesteryl carbamate gives carbon dioxide, cholesterol, cholest-3,5-diene, and *sym*-dibenzylurea. A mechanism of formation of these products is discussed.

During the course of a previous investigation (5) of the preparation of N-substituted-3-aminocholest-5-enes it was noted that Bergmann and Haskelberg (1) had reported the formation of 3-anilinocholest-5-ene by heating cholesteryl chloroformate with methylaniline. If this latter reaction had occurred it would have offered a simple method of preparation of N-substituted-3-aminocholest-5-enes. However, all attempts to repeat this work were unsuccessful. On the other hand, it was found that cholesteryl chloroformate combines with primary and secondary amines to give practically quantitative yields of N-substituted cholesteryl carbamates (I). In this manner Verdino and Schadendorff (6) and Kucherov and Kocheshkov (2) have prepared a



I

number of N-aryl cholesteryl carbamates. This method has been changed to recover amines [as the N-substituted cholesteryl carbamates (cf. Table I)] from their dilute aqueous solutions. Since these derivatives are formed rapidly and with ease this procedure provides an excellent method for the identification of biologically important amines often obtained in dilute solution during degradation studies. Also the large increase in molecular weight in transforming methyl-, dimethyl-, ethylamines, etc., into the corresponding N-substituted cholesteryl carbamates is a decided advantage. Thus it is considered that these derivatives will be a distinct asset in assisting in the identification of amines from biological sources.

Wieland, Honold, and Vila (7) first reported the preparation of cholesteryl chloroformate and its thermal transformation to 3-β-chlorocholest-5-ene. The melting point of their product was below the accepted melting point of pure 3-β-chlorocholest-5-ene so this work was repeated. It was found that

[1] *Manuscript received March 23, 1953.*
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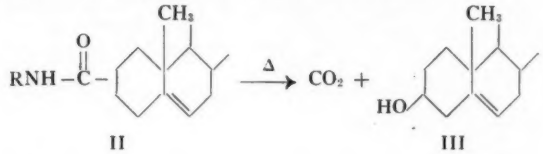
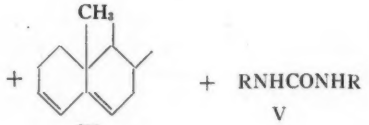
pyrolysis of cholesteryl chloroformate at 150° C. gives a quantitative yield of carbon dioxide and about 20% hydrogen chloride along with cholesteryl chloride contaminated with unsaturated hydrocarbon. Pure cholesteryl chloride (m.p. 95–96° C.) could only be obtained by chromatographing on alumina. The unsaturated hydrocarbon fractions were not identified. In the pyrolysis of N-benzyl cholesteryl carbamate, cholest-3,5-diene (IV) was identified in the unsaturated hydrocarbon fraction (*vide infra*).

In order to be certain that no rearrangement of N-substituted cholesteryl carbamates to 3-aminocholest-5-enes occurs under any conditions of heating, the thermal decomposition of N-benzyl cholesteryl carbamate (II) was studied in detail. No 3- or 6-benzylaminocholest-5-enes were present in the degradation products of any of the several runs. Instead the products were identified as carbon dioxide, 3-β-hydroxycholest-5-ene (cholesterol) III, cholest-3,5-diene (IV), and *sym*-dibenzylurea. Generally a small quantity (1–10%) of the N-benzyl cholesteryl carbamate (II) was recovered unchanged.



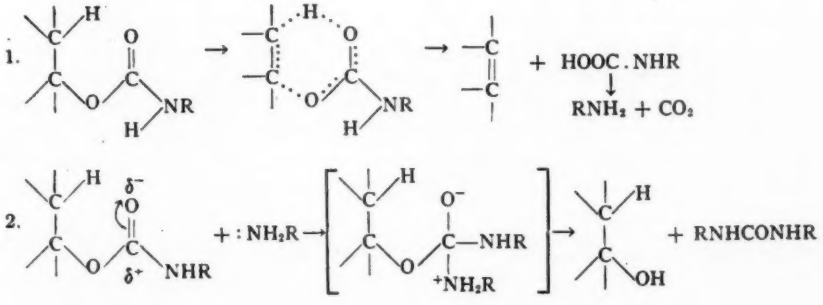
II III



IV V

R = benzyl

If the thermal decomposition of N-benzyl cholesteryl carbamate occurred by the same mechanism as the Chugaev reaction (the thermal decomposition of xanthate esters to produce olefins) then one would expect a good yield of cholest-3,5-diene and no cholesterol [cf. the thermal decomposition of cholesteryl methyl xanthate (3)]. The formation of cholesterol and cholest-3,5-diene together in the pyrolysis of N-benzyl cholesteryl carbamate suggests that two reactions are occurring as follows.



The first reaction, which is pictured with the cyclic transition state similar to that used for the thermal decomposition of cholesteryl methyl xanthate by O'Connor and Nace (3), would produce cholest-3,5-diene, carbon dioxide, and benzylamine, while reaction by the second path would give cholesterol and *sym*-dibenzylurea. If it is considered (without support other than that carbon dioxide is produced in 50% yield and its measurement is quantitative) that both these reactions occur to approximately the same extent, then the products have been obtained from the thermal decomposition of N-benzyl cholesteryl carbamate in the following yields; carbon dioxide (102%), cholesterol (86%), *sym*-dibenzylurea (77%), cholest-3,5-diene (20–40%). The low yields of *sym*-dibenzylurea may be due to partial volatilization of the benzylamine before complete reaction occurred. This is partly corroborated by the slight difference in weight between the weights of starting material and the weights of carbon dioxide plus nonvolatile products. The hydrocarbon, cholest-3,5-diene, was the most difficult product to account for quantitatively. This could be caused by treatment of the ether solution with hydrogen chloride to substantiate the absence of 3- or 6-benzylaminocholest-5-enes.

EXPERIMENTAL[2]

Cholesteryl Chloroformate

Fifty grams of cholesterol was converted into cholesteryl chloroformate (m.p. 119.5–121° C., $[\alpha]_D^{24}$ −26.7) in 86% yield using essentially the method of Wieland *et al.* (7). The acetone mother liquor from the crystallized cholesteryl chloroformate gave a second crop which melted 117.5–119° C. The total yield was 92%.

N-Methyl-N-phenyl Cholesteryl Carbamate

Cholesteryl chloroformate (2.0 gm., 0.004 mole) and methylaniline in 25 cc. of dry acetone were refluxed for two hours. After the solution was cooled and partially evaporated two crops of crystals (m.p. 127.5–131° C.) were obtained, yield 2.35 gm. (100%). One crystallization from acetone raised the melting point to 131–133° C., $[\alpha]_D^{24}$ −6.8. Calc. for $C_{35}H_{53}NO_2$: C, 80.90; H, 10.28; N, 2.69%. Found: C, 80.86; H, 10.36; N, 2.78%.

Treatment of Cholesteryl Chloroformate with Methylaniline

Two grams (0.004 mole) of cholesteryl chloroformate and 1.3 gm. (0.012 mole) of methylaniline on mixing together evolved much heat and crystals were deposited. This mixture was refluxed for three hours under nitrogen. The reaction mixture became homogeneous after 90 min. of heating. The cooled solution was poured into 100 cc. of 10% hydrochloric acid solution after which a very tacky gum separated. This gum was dissolved in hot *n*-butanol as described by Bergmann and Haskelberg (1) for the isolation of cholesteryl aniline. However, although several runs were made, no cholesteryl

[2] *All melting points were determined on a Kofler block. Chloroform was used as a solvent for the optical rotation determinations. Microanalyses were performed by C. W. Beazley, Skokie, Illinois.*

aniline could be obtained from the gum. In some cases a few milligrams of dark solid, which melted at 75–105° C. were obtained.

N-Benzyl Cholesteryl Carbamate

N-Benzyl cholesteryl carbamate (m.p. 148.5–149.5° C., $[\alpha]_D^{24.6}$ −18.7°) was prepared in 89% yield by the method described above for the preparation of N-methyl-N-phenyl cholesteryl carbamate. The melting point reported in the literature (6) for N-benzyl cholesteryl carbamate is 148° C.

N-Alkyl Cholesteryl Carbamates

Method A.—Two mole equivalents of an alkylamine were added to cholesteryl chloroformate dissolved in ether. The heat of reaction was sufficient to reflux the ether. At the end of one hour the lumps of amine hydrochloride were broken up and removed by filtration and washed with ether. The ethereal filtrate and washings on evaporation to dryness gave practically quantitative yields of the N-alkyl cholesteryl carbamates. Generally one crystallization from alcohol was sufficient for purification.

Method B.—Cholesteryl chloroformate (1.0 gm., 0.002 mole) was dissolved in 100 cc. of ether and shaken with 1% aqueous amine (two mole equivalents) solution. The carbamates were isolated by evaporation of the water-washed ether solutions (N-methyl cholesteryl carbamate, which was insoluble in ether, was filtered off, and washed with ether). The crude products were purified by one crystallization from either acetone or 95% ethanol. The N-alkyl cholesteryl carbamates prepared by methods *A* and *B* are listed in Table I.

TABLE I

N-SUBSTITUTED CHOLESTERYL CARBAMATES

Substituents	Method	Yield, %	M.p., °C.	$[\alpha]_D^{24}$	Formula	Carbon		Hydrogen		Nitrogen	
						Calc'd.	Found	Calc'd.	Found	Calc'd.	Found
Methyl	B	95	204–205	−33.0	$C_{29}H_{49}NO_2$	78.50	78.76	11.13	11.20	3.16	2.95
Dimethyl	B	95	112–113	−27.1	$C_{30}H_{51}NO_2$	78.71	78.85	11.24	11.44	3.06	2.77
Ethyl	B	94	161.5–162	−29.0	$C_{30}H_{51}NO_2$	78.71	78.70	11.24	11.38	3.06	2.63
n-Propyl	B	95	141–142	−26.2	$C_{31}H_{53}NO_2$	78.93	78.85	11.33	11.34	2.97	2.74
Isopropyl	B	95	147.5–148.5	−26.8	$C_{31}H_{53}NO_2$	78.93	78.87	11.33	11.36	2.97	2.82
Allyl	B	91	142–143	−23.5	$C_{31}H_{51}NO_2$	79.25	79.05	10.94	11.26	2.98	2.58
n-Butyl	A	99	128–129	−27.6	$C_{32}H_{55}NO_2$	79.11	79.21	11.41	11.32	2.88	3.20
Isoamyl	B	100	128–130	−23.7	$C_{33}H_{57}NO_2$	79.29	79.13	11.49	11.42	2.80	2.70

Pyrolysis of Cholesteryl Chloroformate

Four grams (0.009 mole) of cholesteryl chloroformate were intimately mixed with a 10-fold quantity of finely ground Pyrex glass and placed in a flask. After all the air had been displaced from the apparatus with nitrogen, the outlet was connected to a gas absorption train containing a silver nitrate – dilute nitric acid solution in a wash-tower, a U-tube of Drierite, and a weighed U-tube charged with Ascarite and magnesium chlorate. The flask containing the cholesteryl chloroformate was placed in an oil bath preheated to 160° C. and the temperature was maintained at 150 ± 5° C. for two hours. A slow stream of nitrogen was introduced into the apparatus during the reaction

period. At the end of this time 0.375 gm. (96%) of carbon dioxide had been evolved and 0.248 gm. (equivalent to 20% of the chlorine of cholesteryl chloroformate being evolved as hydrogen chloride) of silver chloride was precipitated.

The residual mixture of glass and pyrolysis product was refluxed with acetone (50 cc.), filtered while hot, and the glass washed with ether. Evaporation of the solvents gave 3.5 gm. of solid (m.p. 73–79° C.). A portion (0.505 gm.) of this product was chromatographed on 20 gm. of alumina in a 24 mm. tube using 50 ml. portions of *n*-pentane as the eluant. It was found necessary to run a second chromatogram on this material. This procedure gave 212.2 mgm. (40.7%) of crude 3-β-chlorocholest-5-ene (m.p. 91–95° C.). One crystallization from acetone raised the melting point to 94.5–95.5° C., yield 90 mgm. This product did not depress the melting point of an authentic sample of 3-β-chlorocholest-5-ene. The remaining fractions from the chromatograms were oils or oily solids.

Thermal Decomposition of N-Benzyl Cholesteryl Carbamate

This was carried out in the same way as the decomposition of cholesteryl chloroformate. Forty grams of finely powdered Pyrex (to pass 28 mesh) and 4.0 gm. (0.0077 mole) of N-benzyl cholesteryl carbamate were intimately mixed and heated together for one hour at 290 ± 10° C. by immersion in a potassium nitrate – sodium nitrite bath. During the heating 0.174 gm. (51%) of carbon dioxide was evolved. After cooling, the organic material was extracted from the glass with hot chloroform and alcohol in turn. These solutions were combined, taken to dryness under nitrogen, and finally dried in a vacuum desiccator. The tan solid (3.8 gm.) was triturated with 50 cc. of absolute ether and the insoluble material recovered, yield 0.68 gm. (74%). This solid melted at 170–171° C. alone and on admixture with an authentic sample of *sym*-dibenzylurea. The ethereal filtrate was shaken with 10% hydrochloric acid and washed with 10% sodium bicarbonate solution and water. The organic layer was evaporated under nitrogen and dried *in vacuo*. This residue on treatment with 50 cc. *n*-pentane gave a white solid, yield 0.85 gm. (m.p. 124–141° C.). Treatment of this solid in the usual manner with digitonin gave a digitonide from which 0.54 gm. of cholesterol (m.p. 144.5–146.5° C.) was recovered. One recrystallization from 95% alcohol raised its melting point to 147.5–148.5° C. which was not depressed by mixture melting point with authentic cholesterol. The filtrate from the digitonide was treated to remove excess digitonin and then taken to dryness. Trituration of the residue with petroleum ether (30–60° C.) yielded a further 0.02 gm. (2.1%) of *sym*-dibenzylurea (m.p. 170.5–171.5° C.) and 0.03 gm. of unchanged N-benzyl cholesteryl carbamate (m.p. 147.5–148.5° C.) which was identified by mixed melting point.

The pentane solution was taken to dryness leaving a residue of 2.1 gm. This was redissolved in 50 cc. pentane and an aliquot containing 1.0 gm. chromatographed on 30 gm. of alumina (Alcoa, F-20, neutralized and reactivated). This column was washed with 100 cc. portions of solvent (cf. Table II).

TABLE II

LIQUID CHROMATOGRAM

Fraction No.	Solvent*	Residue (mgm.)	M.p. (°C.)
1	P	193.7 (557.9)**	70–74 (70.5–75.5)**
2	P	61.8 (26.9)**	Oil (67.5–70.0)**
3–11	P, P.E. to B	35.0	Oils
12–17	B	153.2	Semisolids
18–21	B–E (9: 1)	195.7	From 115° to 137°
22	B–E (9: 1)	38.6	133–140°
23–29	B–E (9: 1 to 1: 1)	163.5	125–135°
30–39	E, E–C, C–A (9: 1 to 1: 1)	207.9	Dark oils

* *P = pentane, P.E. = pet. ether (65–68°), B = benzene, E = ether, C = chloroform, A = acetone.*

** *The values in parentheses refer to another run made essentially to obtain a better value on the yield of cholest-3,5-diene.*

Fraction 1 on crystallization from 5.3 cc. of ethyl acetate – methanol (3: 1) yielded 390 mgm. of crystals (m.p. 78.5–80.0° C., $[\alpha]_D^{23}$ −112°). Another recrystallization gave material melting at 78.5–79.5° C., $[\alpha]_D^{23}$ −116 and $\lambda_{max}^{alc.}$ 235 mμ. Anal. calc. for $C_{27}H_{44}$: C, 87.97; H, 12.03%. Found: C, 87.83; H, 12.44%. The constants reported for cholest-3,5-diene are m.p. 80–81° C., $[\alpha]_D^{20}$ −129.6 (4), λ_{max} 235 mμ (8).

Fraction 2 recrystallized in the same manner gave 9 mgm. of solid which melted at 73–78° C.

Fractions 3–11 and 30–39 resisted all attempts at purification.

Fractions 12–17 were recrystallized from acetone to give 32 mgm. of N-benzyl cholesteryl carbamate (m.p. 145–147° C.) identified by mixture melting point.

Fractions 18–29 were also recrystallized from acetone to yield 123.4 mgm. of cholesterol (m.p. 147.5–149.0° C.) which was identified by a mixture melting point with authentic cholesterol.

REFERENCES

1. BERGMANN, E. and HASKELBERG, L. J. Chem. Soc. 1. 1939.
2. KUCHEROV, V. F. and KOCHESHKOV, K. A. J. Gen. Chem. (U.S.S.R.), 16: 1137. 1946.
3. O'CONNOR, G. L. and NACE, H. R. J. Am. Chem. Soc. 74: 5454. 1952.
4. SPRING, F. S. and SWAIN, G. J. Chem. Soc. 83. 1941.
5. VAVASOUR, G. R., BOLKER, H. I., and MCKAY, A. F. Can. J. Chem. 30: 933. 1952.
6. VERDINO, A. and SCHADENDORFF, E. Monatsh. 65: 141. 1935.
7. WIELAND, H., HONOLD, E., and VILA, J. Z. physiol. Chem. 130: 326. 1923.
8. WOODWARD, R. B. J. Am. Chem. Soc. 64: 72. 1942.

NOTE

A NEW SYNTHESIS OF URANIUM TRIFLUORIDE*

By O. J. C. Runnalls

The compound uranium trifluoride is difficult to prepare. The attempts to synthesize uranium trifluoride have been summarized recently by Katz and Rabinowitch (3). They describe two successful methods.

(*a*) Uranium tetrafluoride is reduced at 1000°C. with rigorously-purified hydrogen (6). The reaction proceeds according to

$$2UF_4 + H_2 \longrightarrow 2UF_3 + 2HF. \qquad [1]$$

Traces of moisture and oxygen must be removed from the apparatus before use by thorough degassing, to prevent the contamination of the product by uranium dioxide.

(*b*) Uranium tetrafluoride is reduced at 1050°C. with finely-divided uranium (2, 7) prepared from the decomposition of uranium hydride.

$$3UF_4 + U \longrightarrow 4UF_3. \qquad [2]$$

The reaction is complete after two hours in an argon atmosphere.

According to the available thermodynamic data, it should be possible to prepare uranium trifluoride by the aluminum reduction of uranium tetrafluoride at a high temperature by the reaction

$$3UF_4 + Al \longrightarrow 3UF_3 + AlF_3. \qquad [3]$$

Aluminum trifluoride could be removed by sublimation in vacuum to obtain an aluminum-free product. However, uranium trifluoride begins to disproportionate at 1000°C.

$$4UF_3 \longrightarrow 3UF_4 + U. \qquad [4]$$

This reaction is accelerated by the sublimation from the system of volatile uranium tetrafluoride. Obviously, the uranium trifluoride would be contaminated with finely-divided uranium which would ignite on exposure to air, forming uranium dioxide.

Klemm and Voss reported (4) that the monofluoride of aluminum volatilized from a mixture of aluminum and its trifluoride when heated above 700°C. in vacuum. Their X-ray results indicated that aluminum monofluoride was stable only in the gaseous state and disproportionated on condensation.

$$3AlF \longrightarrow AlF_3 + 2Al. \qquad [5]$$

If aluminum monofluoride were more volatile than aluminum trifluoride, as has been predicted by Brewer (1), the synthesis of uranium trifluoride free of aluminum should proceed at a temperature where uranium trifluoride is stable and uranium tetrafluoride relatively nonvolatile.

$$UF_4 + Al \longrightarrow UF_3 + AlF. \qquad [6]$$

Experimental reductions have been carried out using the stoichiometric amounts of uranium tetrafluoride and aluminum satisfying the above equation.

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The uranium tetrafluoride was prepared by the hydrofluorination of uranium dioxide at 650°C. "Super-pure" aluminum filings (− 28 to + 60 mesh) were intimately mixed with 3-4 gm. of uranium tetrafluoride. The mixture was heated in a graphite crucible by a tungsten coil surrounded with molybdenum radiation shields, in vacuum. At a crucible temperature of 800°C. a black condensate slowly appeared on the surface of the pyrex flask containing the furnace assembly. At 900°C., the evolution of gas was rapid and ceased after 1.5 hr. After the product had cooled in vacuum it was easily removed from the crucible as one sintered, black mass. The weight loss of the original charge indicated that the gas evolved during the reaction was, in fact, aluminum monofluoride (see Table 1). Further, a chemical analysis of the sublimate yielded an Al:F ratio of 1.09:1.

TABLE I

WEIGHT LOST ON HEATING URANIUM TETRAFLUORIDE AND ALUMINUM TO 900°C.

Experiment	Charge		Reduction time	Theoretical weight loss, gm.		Experimental weight loss, gm.
	UF_4,gm.	Al, gm.		Calculated as AlF	Calculated as AlF_3	
1	3.8646	0.3318	1.5 hr.	0.5655	1.0330	0.5671
2	3.6162	0.3105	1.5	0.5292	0.9667	0.5463
3	4.0285	0.3459	1.5	0.5896	1.0769	0.6035
4	3.5172	0.3020	1.5	0.5148	0.9403	0.5320
5	4.7552	0.4083	2.0	0.6959	1.2712	0.7403

The theoretical weight percentage of uranium in uranium trifluoride is 80.7. Samples from experiments 3 and 4 were analyzed at 80.2% and 80.7% uranium respectively. The major contaminant of uranium trifluoride prepared in the above manner is likely to be uranium dioxide. X-ray powder diffraction patterns of samples 3 and 4 revealed only uranium trifluoride lines, thus limiting any contamination by uranium dioxide to less than 2%. Further evidence supporting a high chemical yield in the process resulted from a chemical analysis for uranium trifluoride using a recently published method by Manning, Miller, and Rowan (5). The method is based on a determination of the total reducing power of the sample. The latter prepared several uranium trifluoride samples by reaction 2, the purest analyzing at about 91% uranium trifluoride. By comparison, our samples 3 and 4 were analyzed at 89.2% and 90.7% uranium trifluoride respectively. It is reasonable to assume that this analytical method may indicate a total uranium fluoride content lower than the absolute percentage present.

ACKNOWLEDGMENT

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1. BREWER, L. Chemistry and metallurgy of miscellaneous materials: thermodynamics. N.N.E.S., IV-19B. Edited by Quill, L. L. McGraw-Hill Book Company, Inc., New York. 1950, p. 197.
2. CHIOTTI, P. and RAEUCHLE, R. U.S.A.E.C. Rept. CC-1525. 1944.

3. KATZ, J. J. and RABINOWITCH, E. The chemistry of uranium. N.N.E.S., VIII–5. McGraw-Hill Book Company, Inc., New York. 1951. p. 349.
4. KLEMM, W. and VOSS, E. Z. anorg. u. allgem. Chem. 251: 233. 1943.
5. MANNING, D. L., MILLER, W. K., and ROWAN, R. U.S.A.E.C. Rept. ORNL–1279. 1952.
6. SPENCER-PALMER, H. J. Brit. Atomic Energy Rept. BR–422. 1944.
7. WARF, J. C. U.S.A.E.C. Rept. AECD–2523. 1949.

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